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THE CHEMISTRY OF CORN OIL.

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DETERMINATION OF THE CONSTANTS.

THE samples of corn oil, the determination of whose constants has been reported in the present article, are here designated as Nos. I, II, and III.

Oil No. I is a commercial article, bought of a reputable dealer and intended for use in the manufacture of cheap paints. It has been kept in a corked tin can for six to seven years. It is of a bright, golden yellow color, is free from foots, and has a pronounced grain-like odor.

Oil No. II is a sample freshly prepared by hydraulic pressure and is of undoubted purity. Its color is somewhat lighter and its grain-like odor more marked than that of oil No. I.

Oil No. III is a product of the mash of distilleries. It is golden brown in color and from ten to twelve years old. The properties of this oil have been so affected by the process of manufacture that it is practically distinct from the other samples examined. For this reason and because this method of manufacture is now obsolete, its examination was dropped at an early stage.

DETERMINATION OF PHYSICAL CONSTANTS.

A. Specific Gravity.

Both the Sprengel tube and the Westphal balance were used in making this determination, although but little reliance can be placed on the latter beyond the second place of decimals.

Results Obtained:

OIL NO. I.

	Wt. water 15.5° C. Grams.	Wt. oil 15.5° C. Grams.	Wt. oil at 100° C. Grams.	Sp. gr. 15.5° C.	Sp. gr. 100° C.
1	1.5265	1.4068	1.3315	0.9216	0.8722
2	1.6404	1.5113	1.4297	0.9213	0.8715
3	1.3602	1.2528	1.1848	0.9210	0.8710
Average for Sprengel tube				0.9213	0.8716
Westphal balance				0.921	0.895

OIL NO. II.

1	2.0130	1.8547	1.7554	0.92136	0.87203
2	2.1788	2.0072	1.8958	0.92124	0.87011
Average for Sprengel tube				0.9213	0.87107
Westphal balance				0.921	.....

OIL NO. III.[1]

1	1.0037	0.9288	0.8789	0.9253	0.8746
2	1.5718	1.4551	1.3780	0.9257	0.8767
Average for Sprengel tube				0.9255	0.8756
Westphal balance				0.9255	.....

Comparison with Results of Other Observers.

Sp. gr. at 15° C.	Observer.	Reference.
0.8360	Rokitianski[2]	*Ph. Russ.* (1894), 712–713.
0.9160	Curtmann	*Chem. Centrbl.*, **59**, 1193.
0.9170	Bowers[2]	*Pharm. J.*, Nov., 1889.
0.9200	Shuttleworth	*Pharm. J.*, **16**, 1095.
0.9215	Schaedler	*J. Soc. Chem. Ind.*, **11**, 504.
0.9216	Procter	*J. Soc. Chem. Ind.*, **17**, 11.
0.9215–0.9244	De Negri and Fabris	*Ztschr. anal. Chem.*, **33**, 547–72.
0.9220	Trimble	*Am. J. Pharm.*, **58**, 265.
0.9239	Hart[3]	*Chem. Ztg.*, **17**, 1522.
0.9238–0.9262	Hopkins	*This Journal*, Dec., 1898.
0.9243	Dulière	*J. Pharm.* (1897), 217.
0.9244	Smith	*J. Soc. Chem. Ind.*, **11**, 504–5.
0.9245	DeNegri[2]	*Chem. Ztg.*, **22**, 961-976.
0.9262	Mills	*J. Soc. Chem. Ind.*, **11**, 504–5.

[1] Fifteen-year-old sample of oil from mash of distillery.
[2] Petroleum ether extract. [3] Dark brown oil.

B. Viscosity.

This determination was made by means of a Boverton-Redwood viscosimeter and the instrument standardized for both distilled water and rape oil at 20° C.

Results Obtained:

	Temperature.	Av. time of flow. Seconds.	Viscos. water.	Viscos. water.
Distilled water	20°	29	1.00	.....
Rape oil	20°	405.5	....	100.00
Oil No. I	20°	283.7	9.79	70.42
Oil No. II	20°	297.7	10.27	73.89

Comparison with Results of Other Observers:

Temperature.	Viscos. water.	Viscos. rape.	Observer.	Reference.
18° C.–19° C	....	61.1	Smith	*J. Soc. Chem. Ind.*, **11**, 504.
15° C.	19.2	...	Andés	"Veg. Fats and Oils."
Viscosity of almond oil			Shuttleworth	*Pharm. J.*, **16**, 1095.
Viscosity greater than olive			Bowers	*Pharm. J.*, Nov., 1889.

C. Index of Refraction.

The instrument used for this determination was Abbé's refractometer.

Results Obtained:

	Temperature.	A.	T.
Oil No. I.			
1	15° C.	1.4768	35.8
2	15° C.	1.4766	36.0
3	20° C.	1.4762	35.9
4	20° C.	1.4760	35.9
Average for	15° C.	1.4767	35.9
Average for	20° C.	1.4761	35.9
Oil No. II.			
1	15° C.	1.4765	35.8
2	15° C.	1.4766	36.0
3	15° C.	1.4767	36.0
Average for	15° C.	1.4766	35.9
Oil No. III.			
1	19.5° C.	1.4767	36.2
2	20° C.	1.4766	36.2
3	20.5° C.	1.4764	36.3
Average for	20° C.	1.4765	36.2

Comparison with Results of Other Observers :

Temperature.	Refractive index.	Observer.	Reference.
15° C.	1.4765	Proctor	*J. Soc. Chem. Ind.*, **17**, 11.

DETERMINATION OF CHEMICAL CONSTANTS—QUANTITATIVE.

A. Free Acid.

The method given in Allen's "Commercial Organic Analysis," II (I), 104, was used in this determination, substituting a mixture of 9 parts neutral alcohol and 1 part ether for the methylated spirit. The percentage of free acid was calculated to oleic acid.

Results Obtained :

OIL NO. I.

	Wt. oil. Grams.	Vol. N/10 KOH. cc.	Acid value.	Free acid. Per cent.	Degrees acidity.
1	10.6617	7.0	3.68	1.851	6.56
2	7.2552	4.8	3.71	1.851	6.62
Average			3.70	1.851	6.59

OIL NO. II.

1	9.9294	4.0	2.26	1.136	4.03
2	13.0816	5.2	2.23	1.121	3.97
Average			2.25	1.128	4.00

OIL NO. III.

1	4.2351	15.6	20.64	10.387	36.83
2	6.2726	23.1	20.66	10.385	36.83
Average			20.65	10.386	36.83

Comparison with Results of Other Observers :

Free acid. Per cent.	Observer.	Reference.
0.75	Hart	*Chem. Ztg.*, **17**, 1522.
0.88	Lloyd	*Chem. Centrbl.*, **59**, 257.
0.00	Spüller	Ding. *poly. J.*, **264**, 626.
5.65	De Negri	*Chem. Ztg.*, **22**, 961-976.

B. Iodine Absorption Hübl Figure.

Necessary Solutions.—

1. $HgCl_2$ in 95 per cent. alcohol, 60 grams per liter.
2. Iodine in 95 per cent. alcohol, 50 grams per liter.

The alcohol used was purified by oxidation with potassium permanganate and subsequent distillation over calcium carbonate. The distillate was rejected until no discoloration was

shown on heating a small portion with a lump of solid potash for ten minutes.

3. N/10 sodium thiosulphate.

4. Twenty per cent. solution of potassium iodide in distilled water.

5. Solution of boiled starch as indicator.

Process.—Thin Erlenmeyer flasks, having accurately fitted ground-glass stoppers and flaring mouths, thus forming a gutter between flask and stopper, were used for this operation.

Equal parts of solutions 1 and 2 were mixed twenty-four hours before each test and allowed to stand in the dark until needed. About 0.250 gram oil was weighed into a test flask, the oil dissolved in 10 cc. chloroform, and 25 cc. of the mixed Hübl solution added. The excess of Hübl solution was afterward found to be about 100 per cent. The flask was then stoppered, the gutter filled with potassium iodide solution, and the whole set away in the dark for twenty-four hours. A blank was run for every determination.

After twenty-four hours the stopper was removed, sufficient potassium iodide solution added to the contents of the flask to prevent any precipitation of mercuric iodide and enough distilled water to make the bulk convenient for titration. The liquid was then titrated with N/10 sodium thiosulphate, starch indicator.

Results Obtained:

OIL NO. I.

	Wt. oil. Gram.	Vol. hypo. cc.	Wt. iodine. Gram.	Iodine absorption. Per cent.
1	0.1986	18.9	0.235323	118.44
2	0.2466	23.7	0.295088	119.66
3	0.2677	26.0	0.323725	120.90
4	0.22835	22.0	0.273921	119.95
Average Hübl figure				119.74

OIL NO. II.

1	0.2708	26.2	0.322183	118.97
2	0.2441	23.3	0.290108	118.85
3	0.2697	25.7	0.319990	118.65
4	0.3070	29.1	0.326232	118.02
Average Hübl figure				118.62

OIL NO. III.

	Wt. oil. Gram.	Vol. hypo. cc.	Wt. iodine. Gram.	Iodine absorption. Per cent.
1	0.2199	20.1	0.250264	113.80
2	0.2894	26.2	0.326215	112.72
3	0.2559	23.4	0.291352	113.85
4	0.2453	22.2	0.276471	112.70
Average Hübl figure				113.27

Comparison with Results of Other Observers:

Hübl figure.	Observer.	Reference.
75.8	Rokitianski	*Ph. Russ.* (1894), 712–713.
111.2–123	De Negri and Fabris	*Ztschr. anal. Chem.*, **33**, 547–72.
115.17	De Negri	*Chem. Ztg.*, **22**, 961–976.
116.3	Smetham	*Analyst*, **18**, 191–193.
117	Hart	*Chem. Ztg.*, **17**, 1522.
119.6	Hazura	*Ztschr. angew. Chem.* (1888), 696.
119.4–119.9	Spüller	Ding. *poly. J.*, **264**, 626.
121.7–122.7	Lane	*J. Chem. Soc.* (1893), A, 153.
122	Hehner	*J. Soc. Chem. Ind.*, **16**, 87.
122	Wallenstein	*Chem. Ztg.* (1894), **18**, (ii), 119.
121.5–123.1	Hopkins	This Journal, Dec., 1898.
122.55	Dulière	*J. Pharm.* (1897), 217.
122.9	Mills	*J. Soc. Chem. Ind.*, **11**, 504.

C. Saponification Value (Koettstorfer Figure).

The method here employed was that given in Allen's "Commercial Organic Analysis," II (I), 56–57. The alcohol employed was prepared as described under "Iodine Values," and a blank run side by side with the test for each determination.

Results Obtained:

OIL NO. I.

	Wt. oil. Grams.	Vol. N/HCl. cc.	Koettstorfer fig.	Sapon. equiv.	Ether value.
1	2.0127	6.95	193.71	289.61	190.01
2	2.5187	8.60	191.55	292.88	187.85
3	2.4600	8.45	192.70	291.13	189.00
Average			192.65	291.21	188.95

OIL NO. II.

1	3.8356	13.20	193.07	290.57	190.82
2	5.2317	18.05	193.55	289.85	191.30
3	2.5611	8.75	191.31	293.24	189.06
Average			192.64	291.22	190.39

OIL NO. III.

1	1.9700	6.75	190.29	294.81	169.64
2	2.2206	7.65	193.26	290.28	172.61
Average			191.78	292.55	171.13

Comparison with Results of Other Observers:

Koettstorfer fig.	Sapon. equiv.	Observer.	Reference.
182.81	306.9	De Negri	*Chem. Ztg.*, **22**, 961–976.
188.1–189.2	298.3–296.6	Spüller	Ding. *poly. J.*, **264**, 626.
188–193	298.4–290.7	De Negri and Fabris	*Ztschr. anal. Chem.*, **33**, 547.
189.5	296	Hart	*Chem. Ztg.*, **17**, 1522.
193.4	290.07	Mills	*J. Soc. Chem. Ind.*, **11**, 504.
198.5	282.6	Smetham	*Anal.*, **18**, 191–193.
198.8–203	282.2–276.4	Dulière	*J. Pharm.* (1897), 217.

D. Insoluble Fatty Acids (Hehner Figure).

From 2 to 4 grams of oil were dissolved in ether in a beaker. Fifty cc. of alcoholic potash (made by dissolving about 20 grams potassium hydroxide in 500 cc. purified and redistilled 95 per cent. alcohol) were added to the ethereal solution and the whole heated on a water-bath until saponification was effected. The liquid was then diluted with hot distilled water and heated until the ether and alcohol were entirely expelled. The aqueous soap solution thus formed was broken up with dilute hydrochloric acid and heating continued until the insoluble fatty acids formed a clear oily layer.

The fatty acids were then washed with boiling distilled water until the filtrate was neutral to methyl orange. An unusual amount of washing was found necessary with this oil, owing to the large proportion of an acid difficultly soluble in hot water. About 1500 cc. of wash-water were used and, as will be seen by the results, the amount of insoluble acids found to be unusually low.

Results Obtained:

OIL NO. I.

	Wt. oil taken. Grams.	Wt. insol. fatty acids. Grams.	Hehner value.
1	4.6700	4.3256	92.63
2	2.6092	2.4121	92.45
3	2.3161	2.1609	93.29
Average Hehner value			92.79

OIL NO. II.

1	3.5853	3.2678	91.14
2	3.2331	3.0142	93.23
3	2.6079	2.4079	92.33
Average Hehner value			92.23

OIL NO. III.

	Wt. oil taken. Grams.	Wt. insol. fatty acids. Grams.	Hehner value.
1	3.9832	3.5102	88.12
2	2.8297	2.4995	88.30
Average Hehner value			88.21

Comparison with Results of Other Observers:

Hehner value.	Observer.	Reference.
93.40	Hoppe-Seyler	*Bull. Soc. Chim.* (1866), [2], **6**, 342.
93.57	Hopkins	This Journal, Dec., 1898.
94.70	Spüller	Ding. *poly. J.*, **264**, 626.
95.70	Hart	*Chem. Ztg.*, **17**, 1522.
96.70	Lloyd	*Chem. Centrbl.*, **59**, 1193.

E. Volatile Acids (Reichert Figure).

Precisely 2.5 grams oil were saponified as in the Koettstorfer process, evaporating off the alcohol completely. Fifty cc. distilled water, containing 1 cc. phenolphthalein indicator, were then added to the dried soap and the whole heated on the water-bath until the soap was completely dissolved. While still warm the aqueous soap solution was titrated with N/2 sulphuric acid, overrunning 2 cc. The total volume of liquid was now 60–65 cc. The decomposed soap solution was then slowly distilled into a similar flask, containing 50 cc of N/10 potassium hydroxide and 1 cc. phenolphthalein indicator. A large percentage of a solid fatty acid also distilled over in white flakes, but was held back by a small wetted filter, placed in the neck of the receiving flask.

When about 50 cc of the liquid in the distilling flask had gone over, 50 cc. of distilled water were added to the residue and the distillation repeated. The contents of the receiver were then titrated back with N/10 hydrochloric acid and the "Reichert figure" calculated from the amount of volatile acids thus recovered from the two distillations.

Results Obtained:

OIL NO. I.

	Vol. N/10 HCl.	Reichert figure.	Wt. KOH for 100 g. oil. Gram.
1	45.8	4.2	0.94248
2	45.6	4.4	0.98736
Average		4.3	0.96492

OIL NO. II.

1	46.0	4.0	0.89760
2	45.6	4.4	0.98736
Average		4.2	0.94248

OIL NO. III.

	Vol. N/10 HCl.	Reichert figure.	Wt. KOH for 100 g. oil. Grams.
1	39.9	10.1	2.26644
2	40.3	9.7	2.17668
Average		9.9	2.22156

Comparison with Results of Other Observers:

Reichert value.	Observer.	Reference.
0.33	Spüller	Ding. *poly. J.*, **264**, 626.
2.5[1]	Smith	*J. Soc. Chem. Ind.*, **11**, 504.
6.7[2]	Morse	*N. H. Expt. Sta. Bull.* (1892), **16**, 19.
0.0	Hopkins	This Journal, Dec., 1898.

F. Acetyl Value.

The method used was that given in Allen's "Commercial Organic Analysis," II (I), 64–65, the "Filtration Process" being the one employed.

Results Obtained:

OIL NO. I.

	Wt. oil. Grams.	Vol. N/HCl. cc.	Koettstorfer fig.	Vol. N/10 KOH. cc.	Acetyl value.
1	2.3420	8.8	210.8	4.5	10.78
2	2.0092	7.6	212.2	4.1	11.45
Average			211.5	..	11.12

OIL NO. II.

1	1.8641	7.1	213.7	3.7	11.14
2	1.4686	5.5	210.1	3.1	11.84
Average			211.9	..	11.49

Comparison with Results of Other Observers:

Koettstorfer fig.	Acetyl value (filtr.).	Observer.	Reference.
201.5	8.25	Lewkowitsch	Allen's "Com. Org. Anal.," Vol. II, 68.
200.9	7.90	Lewkowitsch	Allen's "Com. Org. Anal.," Vol. II, 68.

G. Glycerol.

Hehner's dichromate method, as given in Allen's "Commercial Organic Analysis," II (I), 316–317, was employed for this determination.

Results Obtained:

OIL NO. I.

	Wt. oil. Grams.	Vol. $K_2Cr_2O_7$. cc.	Wt. glycerol. Grams.	Glycerol. Per cent.
1	2.6092	27.57	0.276395	10.59
2	2.3361	24.46	0.245217	10.50
Average				10.545

[1] Calculated. 100 parts oil require 0.56 part KOH.

[2] Calculated. Reported as 3.2 per cent. volatile acids.

OIL NO. II.

	Wt. oil. Grams.	Vol. $K_2Cr_2O_7$. cc.	Wt. glycerol. Grams.	Glycerol. Per cent.
1	2.5701	26.37	0.264359	10.29
2	2.0425	21.21	0.212635	10.41
Average				10.35

H. Phytosterol.

The process of Foster and Reichelmann, as given in the *Analyst* (*1897*), 131, was employed in this determination. The crude phytosterol, resulting from the evaporation of the ethereal extract, was estimated as unsaponifiable matter.

Results Obtained:

	Wt. oil. Grams.	Wt. ether residue. Gram.	Unsap. matter. Per cent.
Oil No. I	55.3945	0.7691	1.39
Oil No. II	49.1123	0.7036	1.43
Average			1.41

Comparison with Results of Other Observers:

Unsap. matter. Per cent.	Observer.	Reference.
1.35	Spüller	Ding. *poly. J.*, **264**, 626.
1.55	Hart	*Chem. Ztg.*, **17**, 1522.
2.86	Hopkins	This Journal, Dec., 1898.

DETERMINATION OF CHEMICAL CONSTANTS—MISCELLANEOUS.

A. Color Reactions with Sulphuric Acid.

I. Heidenreich's Test.—Two drops concentrated sulphuric acid were allowed to fall into the center of 20 drops of oil on a watch-glass. The oil and acid were then stirred together with a glass rod.

Before stirring, all three oils gave a rayed ring of mahogany-red on golden brown background.

After stirring, oils I and II gave a dark red-brown, while oil III gave a dull claret, all of honey-like consistency.

II. Carbon Disulphide Test.—One drop concentrated sulphuric acid was added to a solution of a few drops of oil in carbon disulphide; the mixture was well shaken and allowed to stand.

All three oils gave a fine violet after twenty-four hours.

B. Color Reactions with Nitric Acid.

I. Hauchecorne's Test.—From 3 to 5 parts oil by volume were shaken with 1 part nitric acid (sp. gr. 1.32). The mixture was then

heated on the water-bath for five minutes and allowed to stand.

Oils I and II gave an orange-yellow oily layer of consistency of thick honey.

Oil III gave a mahogany-red layer of much less viscosity.

II. Massie's Test.—Three parts oil by volume were shaken with 1 part nitric acid (sp. gr. 1.42) for two minutes and allowed to stand.

Oils I and II gave a bright mahogany-red oily layer of great viscosity.

Oil III gave a dark, reddish brown layer of less viscosity.

Comparison with Results of Other Observers:

HNO_3.	H_2SO_4.	Observer.	Reference.
Yellow-orange	.....	Dulière	*J. Pharm.* (1897), 217.
.....	Dark red	Hart	*Chem. Ztg.*, 17, 1522.
Reddish (Massie)	Black-brown	Shuttleworth	*Pharm. J.*, 16, 1095.
Reddish yellow	Green	Brannt	"An. and Veg. Fats and Oils."

C. *Silver Nitrate Reduction Tests.*

I. Becchi's Test—Process of Pearmain and Moor.—Ten cc. of oil were shaken with 2 cc. of a reagent prepared by dissolving 1 gram silver nitrate in 100 cc. 95 per cent. alcohol, then adding 20 cc. ether and 1 drop of nitric acid. The mixture was then placed in boiling water for ten minutes.

All three oils gave a dark brown coloration.

II. Brullé's Test.—Twelve cc. of oil were shaken with 5 cc. of a solution prepared by dissolving 2.5 grams silver nitrate in 100 cc. of 95 per cent. alcohol. The mixture was then heated in boiling water twenty minutes.

All three oils were colored intensely black.

Comparison with Results of Other Observers:

Becchi.	Brullé.	Observer.	Reference.
Slightly darkened	.....	Hart	*Chem. Ztg.*, 17, 1522.
Faint brown	Black	De Negri	*Chem. Ztg.*, 22, 961-976.

D. *Elaidin Reaction (Poutet's Method).*

One cc. of mercury was dissolved in 12 cc. of cold nitric acid (sp. gr. 1.42); 2 cc. of the freshly prepared green solution were added to 50 cc. of oil contained in a wide-mouthed, stoppered bottle, the contents of the bottle violently shaken and the agitation

repeated every ten minutes for two hours. The oil was then allowed to stand undisturbed in a warm room.

Results Obtained.—All three oils.

After two hours, orange-yellow deposit, pasty in consistency and small in amount. Orange-red, viscous liquid above.

After two weeks, little change except in gradual darkening of color and decrease in viscosity of supernatant liquid.

Comparison with Results of Other Observers:

Result of test.	Observer.	Reference.
Pasty or buttery mass	Smith	*J. Soc. Chem. Ind.*, **11**, 504.
Orange-yellow color; partial solidification.	Shuttleworth	*Pharm. J.*, **16**, 1095.
Orange-yellow; no solidification.	Dulière	*J. Pharm.* (1897), 217.
Much olein; between olive and cotton-seed oils.	Lloyd	*Chem. Centrbl.*, **59**, 1193.

E. Rise in Temperature with Sulphuric Acid.

In making this determination, Archbutt's method for the Maumené, test, as given in Allen's "Commercial Organic Analysis," II (I), 76–77, was employed. The sulphuric acid used was of 1.842 sp. gr.

Results Obtained:

	Initial temp.	Av. rise in temp.	Specific temp.
Distilled water	23° C.	42° C.	100
Oil No. I	23° C.	75° C.	178.6
Oil No. II	23° C.	74° C.	176.2

Comparison with Results of Other Observers:

Maumené figure.	Observer.	Reference.
56° C.	Spüller	Ding. *poly. J.*, **264**, 626.
60.5° C.	Hart	*Chem. Ztg.*, **17**, 1522.
79° C.	Jean[1]	*J. Soc. Chem. Ind.*, **11**, 504.
84° C.–89° C.	De Negri and Fabris[1]	*Ztschr. anal. Chem.*, 33, 547–72.
89° C.	Mills[2]	*J. Soc. Chem. Ind.*, **11**, 504–5.

F. Heat of Bromination.

The process of Hehner and Mitchell, as given in Allen's "Commercial Organic Analysis," II (I), 80, was followed in making this determination. Six readings were taken for each sample. The calculated iodine value was found by multiplying the bromine thermal value by 5.5.

[1] Obtained by use of Jean's thermelaeometer.

[2] 15 grams oil + 5 cc. H_2SO_4.

Results Obtained:

	Br. Therm. Val.	Hübl No.	Calc. I. No.
Oil No. I	21.9° C.	119.74	120.45
Oil No. II	21.8° C.	118.62	119.90

Comparison with Results of Other Observers:

Br. Therm. Val.	Calc. I. No.	Observer.	Reference.
21.5	118.25	Hehner	*J. Soc. Chem. Ind.*, **16**, 87.

G. Solubility in Glacial Acetic Acid (Valenta's Test).

In this determination the method of Allen's "Commercial Organic Analysis," II (I), 40, was followed. Three cc. of oil and of acid were employed.

Results Obtained:

Oil No. I.—74° C., average of six tests.
Oil No. II.—80° C., average of five tests.
Oil No. III.—44° C., average of five tests.

Comparison with Results of Other Observers:

Turbidity temp.	Observer.	Reference.
65° C.	De Negri[1]	*Chem. Ztg.*, **22**, 961–976.

H. Oxygen Absorption (Livache Test).

Finely divided lead powder was obtained by precipitating metallic lead from lead acetate by means of zinc, washing the precipitate rapidly with water, alcohol, and ether, in the order named, and drying it in a desiccator.

Approximately 1 gram of lead powder, prepared as above, was spread in a thin layer on a large watch-glass and a few drops of oil added by means of a pipette, care being taken to keep the drops of oil separate. The amount of oil taken was accurately determined and was not allowed to exceed 0.6 gram. The watch-glass was then exposed to light but protected from dust and allowed to remain, at the ordinary temperature, until it ceased to gain in weight. All samples tested were examined at the same time and under the same conditions.

[1] Obtained by the use of Jean's thermelaeometer.

Results Obtained:

OIL NO. I.

Wt. oil. Gram.	Total gain. Gram.	Time required. Days.	Gain. Per cent.
0.5193	0.0310	7	5.97

OIL NO. II.

0.3313	0.0172	10	5.19

SUMMARY.

TABLE OF PHYSICAL CONSTANTS.

		Oil No. II.	Oil No. I.	Oil No. III.	Insol. fat acids.
Specific gravity.....	15.5° C.	0.9213	0.9213	0.9255	.....
Specific gravity.....	100° C.	0.8711	0.8716	0.8756	0.8529
Viscosity (water)....	20° C.	10.57	9.79	.....	.....
Viscosity (rape)....	20° C.	73.89	70.42	.....	.....
Index of refraction..	15° C.	1.4766	1.4767	.....	.....
Index of refraction..	20° C.	.....	1.4761	1.4765	.....
Melting-point	.....	.....	.....	.....	22.4° C.

TABLE OF CHEMICAL CONSTANTS—QUANTITATIVE.

	Oil No. II.	Oil No. I.	Oil No. III.	Insol. fat acids.
Per cent. ash	.....	0.065	0.0655	.....
Acid value.....	2.25	3.70	20.65	.....
Per cent. free acid	1.128	1.851	10.386	.....
Degrees acidity	4.00	6.59	36.83	.....
Per cent. iodine absorption..	118.62	119.74	113.27	120.98
Koettstorfer figure	192.64	192.65	191.78	199.15
Saponification equivalent....	291.22	291.21	292.55	281.72
Ether value.....	190.39	188.95	171.13	.....
Hehner value.....	92.23	92.79	88.21	.....
Reichert figure.....	4.2	4.3	9.9	.....
Wt. KOH per 100 grams oil..	0.94248 g	0.96492 g	2.22156 g	.....
Koettstorfer of acetic oil.....	211.9	211.5	.....	.....
Acetyl value.....	11.49	11.12	.....	.....
Per cent. glycerol.....	10.35	10.545	.....	.....
Per cent. unsaponifiable matter	1.43	1.39	.....	.....

TABLE OF CHEMICAL CONSTANTS—MISCELLANEOUS.

	Oil No. II.	Oil No. I.	Oil No. III.	Insoluble fat acids.
Heidenreich—H_2SO_4	Mahogany-red to dark red-brown		Mahogany to claret	....
Carbon disulphide—H_2SO_4	Golden brown; violet after 24 hours.		Claret; violet in 24 hours.	....
Hauchecorne—HNO_3	Orange-yellow		Mahogany	....
Massie—HNO_3	Mahogany-red		Dark red-brown	....
Becchi—$AgNO_3$	Dark brown		Dark brown	....
Brullé—$AgNO_3$	Black		Black	....
Elaïdin test	Orange-yellow deposit; red liquid		Orange solid; dark red liquid	....
Maumené—Rise in temp.	74° C.	75° C.	.....	....
Maumené—Specific temp.	176.2	178.6	.....	....
Bromine thermal value	21.8° C.	21.9° C.	.....	21.6° C.
Valenta's test	80° C.	74° C.	65° C.	....
Livache test—Per cent. gain	5.19 in 10 days	5.97 in 7 days.	.....	....

APPARATUS FOR THE DETERMINATION OF AMMONIA IN WATER, BY THE WANKLYN METHOD, AND TOTAL NITROGEN BY THE KJELDAHL METHOD.

By Robert Spurr Weston.

Received June 12, 1900.

THE introduction of the ammonia method by Wanklyn[1] in 1867 has been followed by many modifications of the original apparatus. Like modifications have followed the introduction of the method introduced by Kjeldahl[2] in 1883.

Wanklyn originally used a tubulated retort and a Liebig condenser. The copper condenser contained a glass tube 90 cm. long and 3 cm. in diameter, thus allowing the beak of the retort to enter the condenser tube. The joint was made by wrapping a little writing paper around the beak of the retort where it entered the condenser tube. Such an apparatus is friable and unhandy.

This single still has been improved upon by various analysts, until there are several forms in use which satisfy most requirements.

An excellent form is described by Cairns[3] and consists of a 2 liter, glass stoppered flask with a side-neck tube. The tube is bent so as to point vertically downward at a convenient distance from the flask. A copper condenser carrying a block-tin zigzag is attached to the neck of the flask by a rubber tube, and the lower end of the condenser is arched upward to prevent the condensed atmospheric moisture from contaminating the distillate. Leffmann[4] makes use of a tubulated retort with a bent neck, connected with a spiral glass worm.

Perhaps the most durable and, all things considered, most convenient form of single still is the one designed by Dr. A. H. Gill and used for several years by Mrs. E. H. Richards in the laboratory of the Massachusetts Board of Health.

This still consists of a flask holding about 1300 cc., which is closed by a cork carrying a $\frac{3}{16}$ inch glass tube. This glass tube is bent so as to enter a $\frac{1}{4}$ inch straight block-tin condenser

[1] Wanklyn: "Water Analysis," 1868.

[2] *Ztschr. anal. Chem.*, **23**, 557.

[3] "Quantitative Analysis," New York, 1896, p. 271.

[4] Leffmann: "Examination of Water," Philadelphia, 1895.

tube. The joint between the glass and tin tubes is made with a cork which is bored half way on one side to receive the glass, and half way on the other side to receive the tin tube. A rubber collar is slipped on to the lower end of the condenser tube to prevent the contamination of the distillate. The condenser is perpendicular and the neck of the flask makes an angle of 45° with it.

This apparatus has many advantages. It is easily boiled clean. Breakage of parts is not frequent, and the broken parts themselves can be replaced at a small cost. The inclined flask is also a decided advantage when the contents have a tendency to bump.

When many stills are used at once, however, these single stills are not so convenient. They take up much bench room unnecessarily, and when the condenser tubes are run through a common cooling tank, the distilling and receiving vessels are on opposite sides and are therefore somewhat inconveniently placed. Perhaps the best arrangement in using a common condenser is that described by Mason.[1]

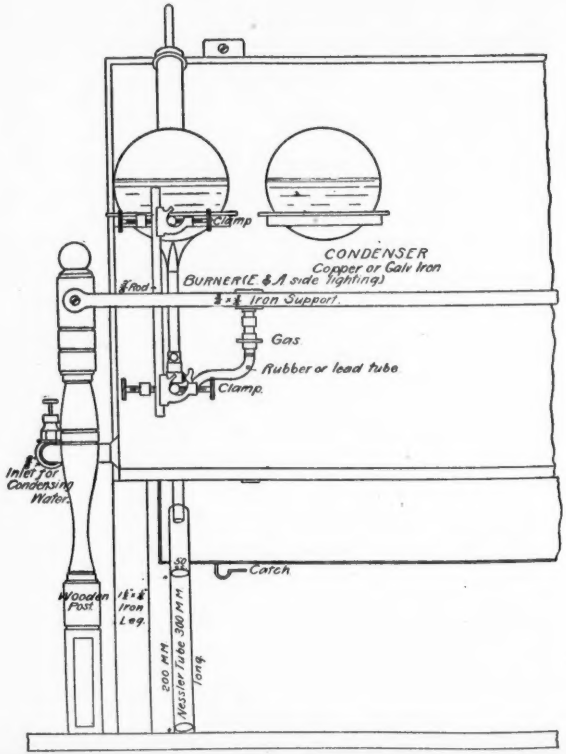
For the determination of nitrogen according to the Kjeldahl method, many forms of still have been introduced. It has been desirable from the beginning, however, to arrange groups of stills. Two forms are in general use.

At the Halle Agricultural Experiment Station an apparatus[2] is used which makes use of an air condenser, but the general arrangement of parts is similar to that used by Mason for water analysis, though Erlenmeyer flasks are used for distilling- and receiving-vessels.

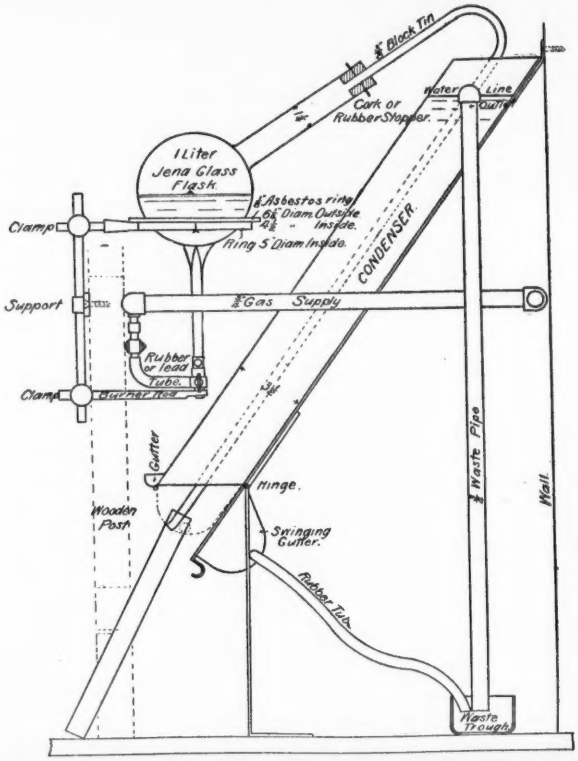
The most important improvements in the construction of sets of stills were made by the chemists of the United States Department of Agriculture, and are described by Professor S. W. Johnson in Bulletin No. 10 of the Division of Chemistry.

This apparatus,[3] of course, is well known and possesses the advantage that it can be operated from one side of the condenser tank. The distilling flasks are raised above the bench, so that it is possible to reach under them for the purpose of attending to the receiving flasks. The distilling flasks are supported upon

[1] "Water Analysis," New York, 1899.
[2] Wiley: "Agricultural Analysis," Vol. II, 203.
[3] *J. Anal. Chem.*, **4**, 179; also Wiley: *loc. cit.*, 208.



FRONT ELEVATION.



SIDE ELEVATION.

an iron shelf. They are joined to the helical block-tin condenser tubes by a safety bulb and rubber connectors. This apparatus was adapted to water analysis by Hazen and Clark.[1]

This apparatus was further improved by the chemists of the Massachusetts Board of Health by bringing the condensing tubes out above the open top of the condenser tank, and by connecting them directly with the stoppers of the distilling flasks, thus avoiding a rubber connection between the distilling flask and the condenser tube. This apparatus was used by the writer for several years, and was found to be quite convenient; nevertheless, some improvements suggested themselves during that time, and in designing a group of ten stills the form described below was developed.

The distilling flasks of the Johnson apparatus are supported on an iron distilling shelf, and the burners are supported on another shelf placed beneath. The metal shelves are hard to keep clean and are, of course, non-adjustable. The distilling flasks, moreover, are placed vertically, and the contents are more liable to be projected into the condenser on that account than if they are inclined. The condenser is unnecessarily large, and the receiving tubes are placed so far under the apparatus as to be inconvenient to tend.

The apparatus described below was designed to overcome the faults of the older apparatus. The drawing on page 470 shows the construction quite plainly. Any desired number of stills can be provided for.

CONDENSER TANK.

The condenser tank is built of copper or galvanized iron. The galvanized iron should be japanned. It is inclined so as to bring the lower ends well forward, and is 7.2 inches in length for each unit. The tank is 3.5 inches thick, and is rhomboidal in section, with sides 2.5 inches and 4.25 inches long respectively. The condenser tubes are of block tin $\frac{3}{8}$ inches in diameter and about 36 inches long. They are straight, not helical. They are soldered into the bottom of the condenser tank, projecting 2 inches below the bottom of the same. They are not supported

[1] Report of Massachusetts Board of Health on "Purification of Water and Sewage," 1890, p. 710.

SIDE ELEVATION.

FRONT ELEVATION.

except at the bottom of the tank, and are sufficiently pliant to allow connection with the flasks to be made with ease.

A swinging gutter is attached to the bottom of the condenser. This gutter can be swung under the condenser tubes when "boiling out" the apparatus. A small upturned gutter is fashioned around the bottom of the tank to catch any possible condensation. The inclined tank brings the tubes well within reach. The tank is supported by legs to the bench and by lugs to the wall.

DISTILLING STAND.

The whole system of flasks and burners is supported by means of a cross bar resting on two or more posts. The $\frac{3}{4}$ inch square, iron cross bar is drilled with holes $7\frac{1}{4}$ inches apart, and $\frac{3}{8}$ inch rods, 10 inches long, are driven into the holes. These rods project 6 inches above and 4 inches below the cross bar. Double clamps hold the rods for the burners and the 5 inch retort stand rings. The base of a Bunsen burner (E and A side lighting) is unscrewed and the burner itself is fitted with a $\frac{3}{8}$ inch rod. The above arrangement permits the flask and the burner to be moved (within limits) in any direction and at will. The flasks are supported by rings of asbestos ($\frac{1}{8}$ inch thick, $6\frac{1}{4}$ inches outside diameter, and $4\frac{1}{2}$ inches inside diameter); these asbestos rings in turn are supported by the iron rings, being secured to the latter by wires. This furnishes a very neat and springy support for the flasks, and one which, to a great extent, relieves the jar due to bumping and the consequent breaking of flasks. A water supply is provided for the condenser, entering near its bottom at one end and wasting near its top at the opposite end. All parts of the apparatus are accessible, and the flasks can be connected and disconnected with one hand, the spring of the condenser tubes helping to hold the stoppers in place.

The gas pipe is supported on the backs of the wooden posts and $\frac{3}{8}$ inch hose cocks are placed to the right of each still support; these cocks are connected with the burners by lead or rubber tubes. Either antimony rubber or selected cork stoppers can be used, the latter, perhaps, to be preferred. The ends of the condenser tube pass directly through the stoppers. If desirable, copper flasks can be used. The writer prefers to use the standard 1-liter, Jena glass round-bottomed flask.

For the determination of nitrogen by the Kjeldahl method it is best to connect the ends of the condenser tubes with glass tubes, the latter to dip into standard acid contained in the receiving vessels. Safety bulbs may also be placed at the tops of the distilling flasks connecting the same with the condenser tubes.

The first set of stills of this design was built for the laboratory of the Cincinnati Water Commission in 1898. It consisted of 10 units. Since that time three other sets have been built, all of which give satisfaction.

To determine the free and albuminoid ammonia in sands and in sewage, it has been found most convenient to place them in a 250 cc. Kjeldahl flask, and to pass through them, by means of a glass tube which should extend nearly to the bottom of the flask, steam from ammonia-free water. This ammonia-free steam is best generated in a closed copper vessel placed at one side of the condenser tank and heated by a large burner. The steam is conducted along the top of the condenser in a $\frac{3}{8}$ inch metal pipe. At suitable intervals $\frac{1}{4}$ inch tees with metal cocks are placed, from which steam can be taken for sand and sewage work.

If desirable, the burners can be easily removed and smaller rings can be used to support the Kjeldahl flasks.

Reagents are added to the flasks by means of a long-stemmed funnel.

A PROCESS FOR THE DETERMINATION OF CARBON DIOXIDE IN CARBONATES.

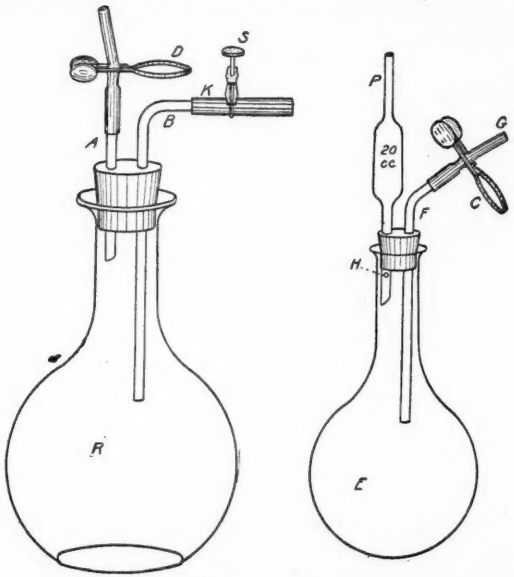
BY R. E. DIVINE.

Received May 28, 1900.

THIS process is based on the principle of Pettenkofer's process; namely, absorption of the carbon dioxide by a measured amount of standard baryta water (solution of barium hydroxide), and titration of the excess of the latter with a standard acid. The apparatus about to be described is simple in construction and may be assembled from materials available in almost every laboratory, and the process, if carried out with a reasonable amount of care, should yield fairly accurate results with anyone. It does not require the time and experience necessary in order to obtain good results by the ordinary gravimetric method.

The apparatus consists of a round-bottomed evolution flask E of about 300 cc. capacity, fitted with a rubber stopper and two tubes P and F, and as a receiving flask a 1 quart Bunsen filtering flask R fitted with two tubes A and B.

P is a 20 cc. pipette cut off so as to leave about 3 inches on each side of the bulb. The lower end is ground to a point on an ordinary grindstone, and at about 1 inch above the point there is



a small hole, H, blown into the side of the tube which enables the condensed drops of liquid to fall freely from the end.

F is a tube bent sufficiently to clear the bulb on P, projecting lower into the flask than P, and fitted on the upper end with a short piece of rubber tube G and a pinch-cock C.

The tube B of the receiving flask is fitted with a piece of heavy pressure tubing K, and a screw-cock S. Tube A is fitted with a short piece of soft tubing and a pinch-cock D.

The empty receiving flask R is first placed on a steam-bath in a place free from draughts and steam generated in a small flask or can (I use an ether can) is passed through A until the flask

is hot, and steam issues through B quite freely. S is now closed tightly, then D, and the apparatus disconnected from the source of steam and placed where it may cool. The evolution flask is now connected with the source of steam at G, and, after the air is expelled and steam issues strongly through P, the rubber tube K of the receiving flask is forced on P, then C is closed and the source of steam disconnected; the apparatus after a minute's cooling is ready to receive the carbonate. This is introduced by placing a small cut-off funnel in the end of G, washing 1 gram of the finely pulverized carbonate into the funnel, then by cautiously opening the pinch-cock C, the carbonate may be completely washed into the flask.

The screw-cock S is now opened wide. Twenty-five cc. of 10 per cent. sulphuric acid[1] are now allowed to flow on the carbonate and E is then heated over a low flame to boiling and boiled until the tube G which has been collapsed by the external pressure swells out nearly to normal size. S is then closed tightly and the heat removed. During the boiling E is allowed to hang supported only by the heavy tube K of the receiving flask. This tends to lessen in great measure the force of bumping in E which takes place as soon as the carbon dioxide is nearly boiled out of the liquid. The boiling must, however, be continued for some time in order to completely displace the carbon dioxide in E by aqueous vapor; E is now disconnected from R at K, and after three or four minutes' cooling 500 cc. of the standard baryta water are allowed to flow into R. This is accomplished without contact with the carbon dioxide of the air in the following manner: An ordinary graduated half-liter flask is fitted with a rubber stopper having three holes. Through one of these passes a tube to the bottom of the flask after the manner of a wash-bottle but fitting closely to the flask so as to remove the contents completely. Through another hole passes loosely a short tube connecting with a wash-bottle containing strong caustic potash solution for washing the air admitted to the flask. Through the remaining hole passes a short tube connecting by means of a long rubber tube fitted with a pinch-cock with a bottle of distilled water on a shelf. The standard baryta solution is of

[1] If the substance forms insoluble sulphates use tartaric acid.

such a strength that 500 cc. require 48 to 50 cc. of half-normal hydrochloric acid for neutralization.

The stopper and tubes are first removed from the measuring flask which is filled with air free from carbon dioxide, and it is then quickly filled to the mark by the siphon on the stock baryta bottle. The stopper is then replaced and the siphon of the measuring flask connected with K of the receiving flask. By opening the screw-cock S the baryta water flows into R. S is closed as the last drops enter the siphon of the measuring flask, the tube connecting with the wash-bottle pulled out of the stopper, and 20 cc. or 30 cc. of distilled water allowed to flow into the flask. This is then sucked over after replacing the wash-bottle connection, and then 20 or 30 cc. more distilled water sucked over in like manner, taking care that not much air enters R which is now shaken thoroughly, and after a minute or two washed air is allowed to enter. The flask is then shaken occasionally for about ten minutes, then air allowed to enter, disconnected from the measuring apparatus, the tubes and stopper rinsed quickly with the jet of distilled water and then immediately titrated with half-normal hydrochloric acid with phenolphthalein as indicator. The acid must not be run in too quickly and the contents of the flask must be thoroughly agitated while the acid is run in so as to avoid decomposition of barium carbonate with loss of carbon dioxide and consequent lowering of the result. The whole process including the standardizing of the baryta solution, weighing the carbonate, etc., can be quite expeditiously carried out and the results are as accurate as those of most technical processes. In working with C. P. sodium carbonate, I have obtained the following figures: 41.33, 41.42, 41.51, 41.32, 41.37, 41.34, and 41.36 per cent. Theory requires 41.51 per cent. Some trials with barium carbonate gave 21.99, 22.05, 21.98, and 21.91 per cent. Theory requires 22.33 per cent.; the barium carbonate contained quite a little chlorine. In this case tartaric acid was used to decompose the carbonate.

Freshly precipitated barium carbonate is sufficiently soluble to give a very faint alkaline reaction to the liquid, and this must be borne in mind if the color returns faintly after titrating.

BUFFALO, May 25, 1900.

[A CONTRIBUTION FROM THE LABORATORY OF THE OMEGO PORTLAND CEMENT CO., JONESVILLE, MICH.]

A METHOD FOR THE RAPID GRAVIMETRIC ESTIMATION OF LIME.

BY W. H. HESS.

Received May 26, 1900.

AN accurate gravimetric determination of lime in cement materials is very important as a check on the calcimeter. The method whereby lime is precipitated as the oxalate, ignited and weighed as the oxide, is both tedious and uncertain since prolonged ignition at a very high temperature is required to completely remove all the carbon dioxide.

The following method of estimation in which the lime is weighed as the sulphate has been found to be rapid and accurate.

The lime in the sample is precipitated and separated as the oxalate in the usual way, and the ignition is carried to the point of removing the filter from the residue of lime. The crucible is allowed to cool partially, when a portion of chemically pure dry ammonium nitrate, approximately equal in bulk to the lime in the crucible, and about twice as much chemically pure fused ammonium sulphate are added. A tight fitting cover is now placed on the platinum crucible and then gentle heat is applied. It has been found very convenient to incline the crucible at an angle of about 30°, allowing the tip of the crucible cover to project outward and then apply the flame to the tip of the cover, gradually bringing the flame under the crucible as the reaction grows less and less violent. The reaction is complete when fumes of ammonia salts are no longer driven off. Intense ignition is unnecessary and is to be avoided. The crucible should be weighed with its cover.

It was found that if ammonium sulphate alone was used, the transposition of carbonate to sulphate of lime was not always complete on first treatment. By the use of ammonium nitrate, easily fusible nitrate of lime is first formed, which is then completely transposed to the sulphate. The ammonium nitrate also helps to complete the ignition of the filter if any remains unburned.

Results on known samples of pure calcium carbonate are as follows:

Weight of $CaCO_3$ taken. Grams.	Weight of $CaCO_3$ recovered. Grams.
0.5003	0.4998
0.4997	0.4993
0.5012	0.5007
0.8472	0.8465
1.0037	1.0026

ON A SYSTEM OF INDEXING CHEMICAL LITERATURE; ADOPTED BY THE CLASSIFICATION DIVISION OF THE U. S. PATENT OFFICE.[1]

By Edwin A. Hill.

Received May 12, 1900.

IN the following paper I will endeavor to describe the system of indexing or digesting chemical literature and patents, now in use in the Classification Division of the United States Patent Office. This division was organized about a year ago to perfect the existing classification of United States patents. Under our laws, no valid patent can be granted for any new process, composition of matter, or chemical body, described in any printed publication prior to the inventor's discovery thereof, or more than two years prior to the date of his application for such patent; and, among other things, this division is now preparing an index or digest of literature and patents relating to chemical bodies and processes, for the use of the office in making its examinations of pending applications.

The system adopted is in the nature of a reference index rather than a classification, and is one elaborated by myself, some five or more years since for another purpose, and on which we have been at work since last summer. I may add that our work was well advanced before my attention was called to the fact that there are great similarities between this system and that of Richter.

Generally speaking, in any comparison of digests or indexes that system may be considered best which, in the simplest, most certain, and most direct manner, puts the inquirer in possession of the desired information.

[1] Read before the Washington Section of the American Chemical Society, May 10, 1900.

If chemical bodies each had but one instead of many names, and if, in chemical literature, one never met with bodies as yet unchristened, then undoubtedly, the dictionary plan, pure and simple, in which the names of bodies were alphabetically arranged and the references to literature and patents were collected under their proper titles, would answer every requirement, and would be, in fact, the only proper system to use.

Practically however, most bodies known to chemists have more than one name, many have several, and the names approved in prior decades are generally not the names in highest repute to-day; nor is it likely that the names now in use will in all, or even in most cases, remain those approved in future years.

Where a chemical compound has several names, were it possible to decide now (which perhaps might be done) which one of them was, on good scientific grounds, the most appropriate in view of present knowledge, and further (which, of course, could not be done), could one be assured that such name would remain the approved name for all future time, such title could, without hesitation, be now adopted as the indexing title, under which all references to literature or patents could be entered, and all other titles and names cross-referenced into it; but, while this might be done now in certain cases, who can guarantee that all the names approved to-day shall retain that approbation as our knowledge of chemical constitution is increased?

Evidently the dictionary plan, unmodified, is not the best, and some better system must be devised not open to these objections.

It would seem that the kind and number of the component atoms of a chemical compound are its most unvarying characteristics, and are subject only to the errors of chemical analysis; and that therefore, these must form the most stable basis for any general scheme for the indexing or digesting of chemical literature; and this conclusion appears to have been independently reached by others than myself; as, for example, by Richter in his recent and former work, and by Jacobsen and Stelzner, following Richter in the index numbers of *Berichte* for 1898 and 1899. We differ chiefly in the methods by which this principle receives practical application.

The simplest, most certain, and most direct system would be to recast the empirical formulas of the compounds, writing

the atoms in the alphabetical order of their chemical symbols, and to then arrange the formulas on an alphabetical basis. For example, take the bodies

$$(CH_3)_2C_2H_2(NO_2)_2,\ (CH_3)_2CHNO_2,\ KH_3C_2O_4,\ CH_3Cl,\ Cu(AsO_2)_2.$$

Rewriting them as above, and arranging them alphabetically, we have

$$As_2CuO_4,\ CClH_3,\ CCl_4,\ C_2H_3KO_4,\ C_2H_7NO_2,\ C_4H_8N_2O_4.$$

It should be noted, however, that the compounds containing C and H, and broadly included in the domain of organic chemistry, constitute so large and important a class that we are fully justified in departing slightly from the alphabetical arrangement of chemical symbols, in order to thereby bring more closely together in the index bodies more or less closely related.

Generally speaking, an attempt to combine a dictionary or digest with a classification will be disastrous. We cannot sit on two stools at once, we will surely fall between them; and too much classification grafted on the dictionary or digest idea will give what is neither a good digest nor a good classification.

Classification, as applied to chemical compounds, should be supplementary to, and independent of, a mere digest or reference index.

In practice, therefore, I have modified the purely alphabetical scheme, and have adopted the following general rule for indexing:

Reject the water of crystallization, and rewrite the empirical formula in the alphabetical order of the chemical symbols, except that in carbon compounds write C first and H second; follow this rewritten formula with the constitutional formula, when given, adding the water of crystallization, if any, but arrange the titles alphabetically by the rewritten formula.

The reason for disregarding water of crystallization may be illustrated as follows: the three bodies, Na_2SO_4 or anhydrous sodium sulphate, $Na_2SO_4 + 10H_2O$ or Glauber's salt, and the heptahydrated salt $Na_2SO_4 + 7H_2O$, are in this way all indexed under the same indexing formula Na_2O_4S, and are thereby brought closely together, as they should be, in one place in the digest. If on the other hand water of crystallization was taken

into account for indexing purposes, the corresponding indexing formulas would become Na_2O_4S, $H_{20}Na_2O_{14}S$, and $H_{14}Na_2O_{11}S$ respectively, and these three very closely related bodies would, in consequence, be widely separated in the digest, which result would, we think, be a very undesirable one.

Our index is being prepared on the card catalogue plan. The cards used are the regular Library Bureau standard card, No. 33, size $7\frac{1}{2}$ by $12\frac{1}{2}$ cm., or approximately 3 by 5 inches, without rulings except a single blue horizontal line, ruled $\frac{3}{8}$ of an inch below the top edge of the card.

The following is a sample set of cards as actually made out in a given instance, except in size.

ONE FORMULA CARD:

$C_{12}O_{18}Fe_2O_{12}$ or $(CH_3.CO_2)_6Fe_2$.

Ferric Acetate; Acetate of Iron; Klaproth's Iron Tincture; Tinctura Ferri Acetatis; Iron Tincture, Klaproth's.

See A Treatise on Chemistry. By H. E. Roscoe and C. Schorlemmer, Vol. 3, Organic Chemistry, Part I, Page 505.

ONE POLYMER OR MULTIPLE FORMULA CARD:

$C_6H_9FeO_6$ Polymer Class 2.

See $C_{12}H_{18}Fe_2O_{12}$ or $(C_6H_9FeO_6)_2$
Ferric Acetate.

TWO CLASSIFICATION CARDS:

Acetates

Ferric.
See $C_{12}H_{18}Fe_2O_{12}$ or $(CH_3.CO_2)_6Fe_2$.

Iron

Acetate of.
See $C_{12}H_{18}Fe_2O_{12}$ or $(CH_3.CO_2)_6Fe_2$.

FOUR SUBJECT-MATTER OR TITLE CARDS:

Ferric Acetate

See $C_{12}H_{18}Fe_2O_{12}$.

Klaproth's Iron Tincture

See $C_{12}H_{18}Fe_2O_{12}$.

Iron, Klaproth's Tincture of

See $C_{12}H_{18}Fe_2O_{12}$.

Tinctura Ferri Acetatis

See $C_{12}H_{18}Fe_2O_{12}$.

Considering first the formula card, it will be noted that in the formula the atoms are rearranged in the alphabetical order of their chemical symbols, except that in carbon compounds C comes first, and H second; and that, had there been water of crystallization in the formula, it would have been rejected. Then follows the constitutional formula, where the water of crystallization, if any, would appear. Thus had the body been cupric acetate, the first line of the formula card would have been

$$C_4H_6CuO_4 \quad \text{or} \quad Cu(C_2H_3O_2)_2 + H_2O.$$

Then follows under the blue ruling, all the names given for the body in question, and finally the reference, by volume and page, to the work indexed.

When a citation is to a patent instead of to a book or other printed work, the reference given will be about like this:

See U. S. Patent No. 319082 to Fahlberg, dated June 2, 1885.

The arrangement of these cards in the card index is strictly an alphabetical one. Thus, all cards reading C_1 take precedence of C_2, C_2 of C_3, etc., etc. In the series C_1, etc., the order of arrangement would be:

$CAgNO$; $CAgS$; CAg_2O_3; CBr; $CClHgN$; CCl_2O; CCl_4; $CCuN$; $CHAgO_2$; $CHBr$; $CHCl_2I$; $CHCl_3$; CH_2AgNO_3S; CH_2Cl_2; CH_2S; CH_3AsCl_2; CH_3Br; CH_3ClOP; CH_3F; CH_4; CH_5AsClO; CH_5ClN; $CH_6AlNO_8S_2$; CH_6ClN; C_2H_2; $C_2H_3CaClO_2$; C_2H_4AgNO; C_2H_6As; $C_6H_4AgNO_2$; $C_9H_{12}O$; $C_{10}H_{16}Cl_2P$; $C_{22}H_{18}ClN_4O$; $C_{40}H_{52}N_4O_{12}S_2$; CdO_4S; $ClCu$; ClH_2Hg_2NO; DiN_3O_9; HKO_3S; $KMnO_4$; PCl_3; PCl_5, etc., etc.

The foregoing series will fully illustrate the method of arrangement.

The polymer or multiple formula cards perform the following function: There are many bodies which analysis shows to be composed of certain elements in certain proportions, but for which theory at present indicates a formula containing two, three, or more times as many atoms. Thus at one time the formula of ferric chloride was written $FeCl_3$, whereas it is now very often written Fe_2Cl_6, and such doubled and tripled formulas are very common.

In all cases where, in the formula as written, the exponents of

all the atoms have a common divisor, after the doubled, tripled, or other form as found is used for preparing the formula card, the formula is then reduced to its lowest terms by dividing the exponents by their greatest common divisor, and a polymer or multiple formula card, made out in the form shown by the foregoing sample ("Class 2," "Class 3," etc., on the polymer cards, indicates the common divisor). In this way the index is rendered independent of any changes in the formula consequent upon future changes of view with reference to constitutional formulas and other matters of theory.

A mere reference index or digest should in no way depend upon any theory subject to future changes with advancing knowledge. Classification, on the other hand, must necessarily depend on theory, and must change as knowledge is increased.

These polymer cards are sorted in with the regular formula cards to form part of the formula division of the index or digest. We may illustrate the function of these cards thus: suppose ferric chloride had been found in the literature under the formula Fe_2Cl_6, and so indexed, but no polymer card made out, and some one consulted the index under the formula $FeCl_3$; the reference, though in the digest, would not be found, but with the polymer card made out the inquirer by it would be referred to the card Fe_2Cl_6, where the required references would appear. All the remaining cards compose the subject-matter or title index, comprised first of the classification cards, second of the regular subject-matter or title cards, and third of any general topics that it may be thought advisable to include in the alphabetical division of the index.

These cards require but little explanation, except that the general statement should be made that all references to the literature or patents of chemical bodies are intended to be entered on the formula card, and all the other cards are merely used as cross references, referring the inquirer to the formula card for all required information.

Classification, it will be noted, is attempted only to a limited extent now, but will be carried out much more completely hereafter, by a supplementary scheme not yet fully perfected — independent of, though based on, the reference index.

The present scheme however, it will be observed, does inci-

dentally, bring together very many closely related carbon and other compounds, and arranges alphabetically, under such general titles as acids, alcohols, ethers, acetates, chlorides, etc., the specific bodies of the given class.

In practice, to use the digest, if the empirical formula of any compound is known, it must be rewritten by the rule already given, and at once is disclosed the definite place in the formula index where the desired references, if digested, will be found entered upon the formula card.

If on the other hand, one of the various names of the body is given, the subject-matter index is entered alphabetically, and a cross reference obtained to the rewritten formula with which the formula index is entered for the required information.

The question arises, as between this system and such a one as that adopted in the *Berichte*, which one of them is the best; that is, the most practical for the intended uses. It may be said generally that the Patent Office needs the index for exactly the same purpose as the scientific or practical chemist; *i. e.*, to obtain references to the literature concerning definite chemical bodies, where either the name or the chemical composition or both is given, so that the system best for the one use is probably also best for the other as well.

We consider our system to be preferable, certainly so at least for the patent office, and I may say that it was elaborated and adopted without any knowledge of the work of Richter as followed in the *Berichte* by Jacobsen and Stelzner.

In our system, the arrangement of the formulas is governed by the following general principles in the following order:

1st. The number of C atoms } in carbon compounds.
2nd. The number of H atoms }
3rd. The alphabetical arrangements of the symbols of the remaining elements (including H in other than carbon compounds).

Practically, in indexing, or in using the digest as an index, the only thing to be remembered is, that in carbon compounds C comes first and H second, and that otherwise the rearrangement of formulas and the arrangement of such formulas in the digest is always alphabetically by the symbols, instead of by the names of the component elements.

That the *Berichte* system is much more complex will be seen at once. Other things being equal, we deem that system which is simplest to be the best, provided it achieves a result of equal value. The ideal system, we think, produces the best result with the minimum of labor, both mental and physical.

In rewriting the empirical formula by the *Berichte* or Richter system, one must remember the following arbitrary established order of precedence of certain of the chemical symbols; *viz.*, C, H, O, N, Cl, Br, I, F, S, P, and this both in rewriting the formulas and in entering the table. One must also consider the number of carbon atoms in the compound, the number of different varieties of atoms, and various other things as well.

Thus for example, in the Richter system, the following are the principles which govern, in the order of their relative importance:

1st. The number of C atoms.

2nd. The number of different kinds of atoms other than C.

3rd. The arbitrary arrangement of ten of the component elements in the following order; *viz.*, C, H, O, N, Cl, Br, I, F, S, P, all taking precedence over the remaining elements.

4th. The arrangement of all other component elements in the alphabetical order of their chemical symbols.

5th. The arrangement of chlorides, bromides, amides, anilides of carbon acids, acetyl and benzoyl derivatives, oximes, phenylhydrazones, etc., under the formulas of their corresponding bases.

6th. The arrangement in general, of salts, either under the formulas of their bases, or of their acids.

7th. The arrangement of salts of quarternary ammonia bases under the formulas of their corresponding hydroxides.

By way of comparison, I have taken from the pages of the *Berichte* index a number of bodies, with the formulas written and arranged as there shown, and have rewritten and rearranged them on our own classification division plan.

FORMULAS TAKEN FROM THE BERICHTE INDEX.

Pages refer to *Berichte*, No. 19, of 1899.

C_1: CO_2, CCl_4, CS_2, CHN — p. 3448.
C_1: $CHCl_3$, $CHBr_3$, CH_2O — p. 3449.
C_1: CH_2N_4, CH_2I_2, CH_3N_5, CH_3Br, CH_4O_3, CH_5N, $COCl_2$, $CNBr$, CHO_2Cl, $CHNS$ — p. 3450.
C_1: $CO_4N_2Br_2$, CHO_4N_2Br — p. 3451.
C_2: C_2H_2 — p. 3452.
C_2: C_2Cl_6, C_2HN_3 — p. 3452.
C_2: $C_2Cl_6Hg_6$, $C_2I_2Hg_2$ — p. 3453.
C_2: C_2HOCl_3, $C_2H_2O_5N_4$, $C_2H_2N_3Cl$, $C_2H_3O_2Cl_3$ — p. 3454.
C_2: $C_2H_3O_2Br$, $C_2H_4O_7S_2$, $C_2H_4N_2Cl_2$ — p. 3455.
C_2: $C_2H_5O_2N$, $C_2H_5N_2Cl_3$, $C_2H_6O_3S$, C_2H_6NBr — p. 3455.
C_2: $C_2HO_2Cl_3Hg_3$ — p. 3456.
C_3: C_3H_6, C_3H_2O — p. 3456.
C_3: $C_3HO_2N_5$, C_3H_3OBr, C_3H_3OCl, C_3H_3OBr — p. 3459.
C_3: $C_3H_6O_4S$, $C_3H_6N_2S$ — p. 3460.
C_3: C_3H_9ON, C_3H_9NS, $C_3H_{12}ON_2$, $C_3H_3O_2N_3S$, C_3H_6ONBr — p. 3461.
C_4: C_4H_4O, $C_4H_{12}N_2$, $C_4N_2Hg_4$, $C_4H_2O_4N_2$ — p. 3464.
C_4: $C_4H_{13}ON$, $C_4H_7ON_3S$ — p. 3466.
C_4: C_5H_{12}, $C_5H_4O_2$ — p. 3466.
C_5: $C_5H_{11}N$, $C_5H_{14}N_2$, $C_5HN_4Cl_3$ — p. 3470.
C_5: $C_5H_2O_3Cl_4$ — p. 3471.
C_5: $C_5H_{15}O_2N$, $C_5H_7ON_4Cl_2$ — p. 3471.
C_6: C_6H_6, C_6H_{14}, C_6Cl_6, $C_6H_2O_6$ — p. 3474.
C_6: $C_6H_6O_2$ — p. 3475.
C_6: $C_6H_6N_4$, $C_6H_6Cl_6$, C_6H_6S — p. 3476.
C_6: $C_6H_{15}P$, $C_6H_3OCl_3$ — p. 3480.
C_6: $C_6H_3NCl_4$ — p. 3480.
C_6: $C_6H_{20}O_2As_2$, $C_6H_2ONBr_3$ — p. 3489.
C_6: $C_6H_{14}O_2NBr$, $C_6H_5OCl_2SP$ — p. 3491.

In the foregoing arrangement, the formulas are given in the same order as in the *Berichte*, other formulas which come in between these being omitted; and in the following table these formulas are rewritten and rearranged on the plan which we have adopted, a few formulas not found in the *Berichte* index being added to illustrate the application of our scheme to inorganic bodies.

FORMULAS REWRITTEN AND ARRANGED ON THE PLAN ADOPTED BY THE CLASSIFICATION DIVISION, U. S. PATENT OFFICE.

The rewritten formula is in our digest generally followed by the empirical or constitutional formula as usually written by chemists, but from lack of space I have omitted the constitutional formula in many cases in the following table:

C_0 Not in *Berichte* Index.

AgCl	
$AgMnO_4$	
$AlH_4NO_2S_2$ or $NH_4Al(SO_4)_2 + 12H_2O$	
AsH_2KO_4 or KH_2AsO_4	
$AuCl_4K$ or $KAuCl_4$	
$BNaO_2$ or $NaBO_2$	
BaN_2O_6 or $Ba(NO_3)_2$	
Br_2OSe or $SeOBr_2$	
Br_2Zn or $ZnBr_2$	

C_1

H_0	$CBrN$ or $Br\,CN$
	$CBr_2N_2O_4$ or $C(NO_2)_2Br_2$
	CCl_2O or $COCl_2$
	CCl_4
H_1	$CHBrN_2O_4$ or $CHBr(NO_2)_2$
	$CHBr_3$
	$CHClO_2$ or $COCl.OH$
	$CHCl_3$
	CHN or HCN
	$CHNS$ or $CN.SH$

C$_1$

H$_2$: CH_2I_2; CH_2N_4; CH_2O or COH_2

H$_3$: CH_3Br; CH_3N_5

H$_4$: CH_4O_3

H$_5$: CH_5N or $NH_2(CH_3)$

H$_n$: CO_2; CS_2

C$_2$

H$_0$: C_2Cl_6; $C_2Cl_6Hg_6$ or $C_2Hg_6Cl_6$

H$_1$: $C_2HCl_3Hg_3O_2$ or $CHg_3Cl_2CO_2H$; C_2HCl_3O or $CCl_3.CHO$; C_2HN_3

H$_2$: C_2H_2; $C_2H_2ClN_3$; $C_2H_2N_4O_8$ or $C_2H_2(NO_2)_4$

H$_3$: $C_2H_3BrO_2$; $C_2H_3Cl_3O_2$ or $CCl_3.CH(OH)_2$

H$_4$: $C_2H_4Cl_2N_2$ or $(CH_2Cl)_2N_2$; $C_3H_4O_7S_2$ or $CHO.CH(SO_3H)_2$

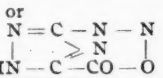
H$_5$: $C_2H_5Cl_3N_2$; $C_2H_5NO_2$ or $C_2H_5NO_2$

H$_6$: C_2H_6BrN or $N(CH_3)_2Br$; $C_2H_6O_3S$ or $C_2H_5(SO_3H)$

H$_0$: $C_2Hg_2I_2$

C$_3$

H$_1$: $C_3HN_5O_2$ or



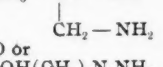
H$_2$: C_3H_2O or $CHO.C_2H$

H$_3$: C_3H_3BrO

H$_5$: C_3H_5BrO; C_3H_5ClO; $C_3H_5N_3O_2S$

H$_6$: C_3H_6 or $CH_3.CH.CH_2$; C_3H_6BrNO or $N.CO.C_2H_5.HBr$; $C_3H_6N_2S$

H$_9$: C_3H_9NO or $OH.CH_2.CH_2.NH.CH_3$; C_3H_9NS or

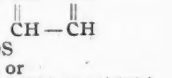


H$_{12}$: $C_3H_{12}N_2O$ or $OH(CH_3)_3N.NH_2$

C$_4$

H$_2$: $C_4H_2N_2O_4$

H$_4$: C_4H_4O or



H$_7$: $C_4H_7N_3OS$

H$_{12}$: $C_4H_{12}N_2$ or $(CH_3)_2N.N(CH_3)_2$

H$_{13}$: $C_4H_{13}NO$ or $N(CH_3)_4OH$

$C_4Hg_4N_2$

C$_5$

H$_1$: $C_5HCl_3N_4$

H$_2$: $C_5H_2Cl_2N_4O$; $C_5H_2Cl_4O_3$

H$_4$: $C_5H_4O_2$

H$_{11}$: $C_5H_{11}N$

H$_{12}$: C_5H_{12} or $CH_3(CH_2)_3CH_3$

H$_{14}$: $C_5H_{14}N_2$

H$_{15}$: $C_5H_{15}NO_2$ or $N(CH_3)_3(C_2H_4.OH)OH$

C$_6$

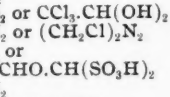
H$_0$: C_6Cl_6

H$_2$: $C_6H_2Br_2NO$; $C_6H_2O_6$

H$_3$: $C_6H_3Cl_3O$ or $C_6H_2Cl_3(OH)$; $C_6H_3Cl_4N$ or $C_6H.Cl_4NH_2$

H$_5$: $C_6H_5Cl_2OPS$ or $SP(OC_6H_5)Cl_2$

H$_6$: C_6H_6; $C_6H_6Cl_6$; $C_6H_6N_4$ or



$C_6H_6O_2$ or $C_6H_4(OH)_2$; C_6H_6S or $C_6H_5.SH$

H$_{14}$: C_6H_{14} or $(CH_3)_2CH.CH(CH_3)_2$; $C_6H_{13}Br$

H$_{15}$: $C_6H_{15}P$ or $P(C_2H_5)_3$

H$_{20}$: $C_6H_{20}As_2O_2$ or $(CH_3)_3(OH)As_2OH(CH_3)_3$

Not in Beilstein Index.

Cl: ClO_3; Cl_2Ni or $NiCl_2$

Co: CoS

Cr: CrO_4Pb or $PbCrO_4$; $Cr_2K_2O_{16}S_4$ or $Cr_2(SO_4)_3K_2SO_4+24H_2O$; CuN_2O_6 or $Cu(NO_3)_2$; $FeKO_8S_2$ or $FeK(SO_4)_2$

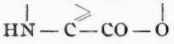
H: HK_2 or K_2H; H_2MoO_4; H_3N or NH_3; $HgNO_3$; IKO_3 or KIO_3; $K_2NiO_8S_2$ or $NiSO_4+K_2SO_4+6H_2O$; MoO_4Pb or $PbMoO_4$; Na_2O_3Si or Na_2SiO_3

O: OPb or PbO; O_2Pd or PdO_2; O_3Te or TeO_3

SSi or SiS

As a practical test of the two systems, take the six following bodies; rewrite them first by our system and find them in our table; then rewrite them by the *Berichte* rules and find them in the *Berichte* table; and the demonstration of the superior simplicity of our system will be complete. The bodies are:

1. ..... $SP(OC_6H_5)Cl_2$
2. ..... $C_6H_2Cl_3(OH)$
3. ..... $CHg_3Cl_3CO_2H$
4. ..... CN.SH
5. ..... $N.CO.C_2H_5.HBr$
6. .....



This comparison speaks louder than words, and I think most chemists will agree with me that our system affords to the inquirer, with the minimum of technical knowledge, the maximum of information, in the surest manner, and with the minimum of mental and physical labor, and without the danger that a future change in theory will mislead the future user of it. In other words, the use of the digest is as far as possible independent of all theory, and founded only on unchanging facts.

Let me here call attention to the point that in the *Berichte* system the formulas of very many large classes of bodies, such as salts, amides, anilides of acids, etc., etc., have no representation in the index. Their formulas do not appear in it at all; but only their names, which are classified under the different formulas of some related body; so that in a given case, unless one remembers all these various classes of excepted bodies, if forgetting any of these things he rewrites the formula, and enters the *Berichte* digest or index with it, thus rewritten, he finds none of the matter indexed. He must first remember that the body sought is not indexed under its own, but under some different formula of a body more or less closely related to it; that is, that the body belongs in some one of these many excepted classes, and then, after determining under what base or acid it will be found, he must enter the table with the rewritten formula, not of the body itself, but of the given base acid or other body to which it is now supposed to be related, although advancing knowledge may hereafter prove this view as to supposed relationship to be erroneous.

Moreover, in the case of a body of which the number and kind of the component atoms are known, but as to the constitution of which little or nothing is known, while the body may be correctly entered in the *Berichte* index under the formula of some base or acid or other supposedly related body, it would evidently never be found, because not knowing its constitution, we do not know the base or acid under which it is indexed, and so would not find it in the table.

In our system, every chemical body indexed is represented in the digest or table by its rewritten empirical formula. No bodies are indexed as subheads under the formulas of other compounds. The indexing, and conversely, the finding of the body in the index, is rendered absolutely independent of any theories of constitution whatever, and made to depend solely on the kind and number of the component atoms, arranged alphabetically by their symbols, except that in carbon compounds, C comes first and H second. Nothing can be more simple.

No serious attempt is made, however, to make the system, which is merely intended to be a reference index, at once a classification, and also an index as well; that is, classification is not pushed beyond the point where it begins to encroach on the digest idea; and any such attempt, I believe, will surely fail to fully fulfil either function in the highest degree. In a good index, the classification idea must be kept subordinate. Hence, it follows that from our point of view, the *Berichte* system, as a mere digest or index, as well as that of Richter and all other similar systems, is inferior to ours in the points indicated; while as systems of classification, they can not but be inferior to such as are founded on proper lines. Such systems can be worked out without being hampered by the digest or dictionary idea, and which important work — classification proper as distinguished from a mere digest or index — we hope to be able to take up at some future time, on a comprehensive scale, as supplementary to the present work in hand.

It would be manifestly unfair, however, in this comparison of systems, to overlook the fact that both in the field covered, and in the intended use, the two systems are not exactly the same. Richter's system is designed for and applied solely to the bodies of organic chemistry for the use of specialists in that branch

familiar with its classification. Ours covers the entire domain of chemical research, both inorganic and organic, and is for the general inquirer. From a classification standpoint, the order of preference — C, H, O, N, Cl, Br, I, F, S, P — is justified in organic chemistry; but in inorganic chemistry it has no justification, and would lead to awkward and unfamiliar formulas, with no compensating advantages.

When a general reference index to all bodies, both organic and inorganic, is under consideration, if an order of preference is to be established, one will have to adopt different orders in the organic and inorganic domains, or else do as we have done — that is, establish no order of preference whatever, with the one exception of giving C and H preference in that order in carbon compounds so as to thereby effect a differentiation of organic from inorganic bodies.

Moreover, Richter's system is more adapted to the needs of those who are studying bodies as a class and to whom classification is of greater importance; while our system is specially adapted to the needs and requirements of those who are merely searching for references to the literature of specific chemical bodies — particularly those bodies the empirical formulas of which are known, but as to the constitution of which little if any information is at hand.

The approval of our system, therefore, does not necessarily imply that it is a criticism of or shall supersede that of Richter. Because of these differences in the field covered and in the intended use, the two systems have really no serious quarrel; and where ours is applied to organic bodies, the Richter formula could also be given on the cards prepared on our system to facilitate reference to the *Berichte*, and the Richter Lexicon, with its 75,000 titles of organic compounds.

In conclusion, there arises the question of how far the system described in this paper is adapted to the needs of chemists generally as a universal scheme for the indexing or digesting of chemical literature. That it fully meets the needs of the Patent Office we have no doubt, and for myself, I can not see why the needs of the practical and scientific chemist are not about the same as ours.

The object of a dictionary of chemistry, a reference index, or

a digest system, such as those contained in the German *Berichte* and similar works, and the *Abstracts* of the Chemical Society, is to furnish to the chemical inquirer, in the best and quickest way, digested information and references to the latest literature on any given chemical body, process, or general chemical topic. Our system directly covers, very fully, and in, we believe, the best and quickest way, the inquiry as to the chemical body, and incidentally, the inquiry as to any specific chemical process, since every such process has for its aim the production of a specific chemical body, and hence the literature relating to such process will, of course, be digested under the formula of the resulting product.

An index or digest of general chemical topics, or processes of a general nature not specially adapted to the production of a specific body, but to many bodies more or less closely related, can not, of course, be included in any mere formula scheme, which can only represent specific bodies, but must come into some general or dictionary plan based on names or titles, and such references of this class as it might seem desirable to include in a general scheme of chemical indexing, would easily work in with the alphabetical arrangement of chemical names provided for in the system we have adopted.

Probably the most natural objection which the practical chemist would make to the adoption of the system of indexing by rewritten formulas as one of the component parts of a general scheme for chemical indexing, would be that to rewrite or rearrange the chemical symbols in the accepted formula on a purely alphabetical basis, would appear to offend the chemical sense, and do violence to the long-established usage of chemists in writing such formulas with the component elements or radicals arranged in an order depending largely on their relative, positive, or negative qualities, using these terms in their broadest chemical meaning.

In answer to this objection, it should be noted that if this really be a valid objection, it applies just as fully to the system used by Richter in the earlier editions of his "Lexicon" and adopted and approved in the *Berichte* Indexes and other publications as to ours; and it can be urged with equal force against the monumental work of Richter, just published, which is an

familiar with its classification. Ours covers the entire domain of chemical research, both inorganic and organic, and is for the general inquirer. From a classification standpoint, the order of preference — C, H, O, N, Cl, Br, I, F, S, P — is justified in organic chemistry; but in inorganic chemistry it has no justification, and would lead to awkward and unfamiliar formulas, with no compensating advantages.

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In conclusion, there arises the question of how far the system described in this paper is adapted to the needs of chemists generally as a universal scheme for the indexing or digesting of chemical literature. That it fully meets the needs of the Patent Office we have no doubt, and for myself, I can not see why the needs of the practical and scientific chemist are not about the same as ours.

The object of a dictionary of chemistry, a reference index, or

a digest system, such as those contained in the German *Berichte* and similar works, and the *Abstracts* of the Chemical Society, is to furnish to the chemical inquirer, in the best and quickest way, digested information and references to the latest literature on any given chemical body, process, or general chemical topic. Our system directly covers, very fully, and in, we believe, the best and quickest way, the inquiry as to the chemical body, and incidentally, the inquiry as to any specific chemical process, since every such process has for its aim the production of a specific chemical body, and hence the literature relating to such process will, of course, be digested under the formula of the resulting product.

An index or digest of general chemical topics, or processes of a general nature not specially adapted to the production of a specific body, but to many bodies more or less closely related, can not, of course, be included in any mere formula scheme, which can only represent specific bodies, but must come into some general or dictionary plan based on names or titles, and such references of this class as it might seem desirable to include in a general scheme of chemical indexing, would easily work in with the alphabetical arrangement of chemical names provided for in the system we have adopted.

Probably the most natural objection which the practical chemist would make to the adoption of the system of indexing by rewritten formulas as one of the component parts of a general scheme for chemical indexing, would be that to rewrite or rearrange the chemical symbols in the accepted formula on a purely alphabetical basis, would appear to offend the chemical sense, and do violence to the long-established usage of chemists in writing such formulas with the component elements or radicals arranged in an order depending largely on their relative, positive, or negative qualities, using these terms in their broadest chemical meaning.

In answer to this objection, it should be noted that if this really be a valid objection, it applies just as fully to the system used by Richter in the earlier editions of his "Lexicon" and adopted and approved in the *Berichte* Indexes and other publications as to ours; and it can be urged with equal force against the monumental work of Richter, just published, which is an

familiar with its classification. Ours covers the entire domain of chemical research, both inorganic and organic, and is for the general inquirer. From a classification standpoint, the order of preference — C, H, O, N, Cl, Br, I, F, S, P — is justified in organic chemistry; but in inorganic chemistry it has no justification, and would lead to awkward and unfamiliar formulas, with no compensating advantages.

When a general reference index to all bodies, both organic and inorganic, is under consideration, if an order of preference is to be established, one will have to adopt different orders in the organic and inorganic domains, or else do as we have done — that is, establish no order of preference whatever, with the one exception of giving C and H preference in that order in carbon compounds so as to thereby effect a differentiation of organic from inorganic bodies.

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enlarged edition of his earlier work. So that, with such backing as Richter and the *Berichte*, it would seem as if the objection was not as valid as might at first appear.

Moreover, in our system it is an unvarying rule that the rearranged formula is never used or written, whether on cards or elsewhere, without being immediately followed by the empirical or constitutional formulas, so far as the same are known or inferred; so that an objection which might have force, were nothing but the rewritten formulas given in the digest or on the index cards, loses its force when the ordinary formula, so familiar to the chemist, is always an invariable accompaniment of the new and unfamiliar indexing formulas.

As soon as the idea is fully grasped that the rewritten formula is merely an arbitrary arrangement, in the nature of a position indicator, determining position in a mere reference index to literature and nothing more, the chemical sense will be no longer offended. The justification for its use lies in the fact that such a formula unerringly indicates one, and one only, definite and specific place in the index where we are to look for all references, with a certainty that no other character, name, or title of the body can afford. With other systems we are somewhat uncertain where to look for our information; — with this system all uncertainty at once disappears.

Personally I should be glad to see a general scheme of indexing current chemical literature carried out at some future time for the benefit of American chemists, under the auspices, for instance, of the Smithsonian Institution, along these general lines which have been blocked out in our Classification Division, modified or improved perhaps by the combined wisdom and experience of the American Chemical Society.

For example, the Smithsonian Institution might publish an annual index to current chemical literature, divided into a formula division, arranged along some such lines as here suggested, and a subject-matter or title division, in which all names and subjects were alphabetically arranged, and the names of chemical bodies all cross-referenced into the formula index, all references to the literature of chemical bodies being collated under the unvarying formula of the body, and not under one of its various and varying names.

Such an index should cover the leading chemical periodicals —such works as *Berichte* and the *Abstracts* of the Chemical Society, and the more important chemical publications of the year.

The vast army of chemical workers in our universities, laboratories, and corporate and government offices and institutions, state and national, should be enlisted in the work, each willing worker assigned some special publication or portion of same, and be supplied with standard library bureau cards and general instructions; and the cards as prepared sent in to the central bureau established here in Washington, where, after being sorted into place in the receiving cabinets, and with proper editing, they would form the basis from which would be compiled the annual index volume.

These volumes would probably be less of a digest and more of an index than the present *Abstracts* of the Chemical Society or the *Berichte*, and would cover a somewhat different field than either.

Lastly, these annual volumes should be sold at cost price, so as to become a working tool in the hands of all the chemical workers of the country.

I may here briefly refer to a special development of this work now being carried out in our Patent Office Index. We have procured two copies each of the *Berichte* Indexes for 1898 and 1899. The separate titles in the formula portion of these indexes are in most cases small enough to be cut out and pasted on our standard indexing cards and still leave room enough at the top to rewrite the formula on our own plan. We are also considering the application of this system of cutting and pasting from two duplicate copies to the new Richter "Lexicon" with its 75,000 titles, and possibly to the four volumes of the last edition of Watts' "Dictionary," Thorpe's "Dictionary of Applied Chemistry," the yearly abstract volumes of the *Journal of the London Chemical Society*, and such other works of general reference as it may be found advisable.

But to return, in conclusion, to the idea of a central bureau at Washington, supervising the indexing of chemical literature, would not some such plan, properly matured, and carried out to a successful completion, be a work worthy of the great scien-

tific institution of the national capitol, founded expressly for the dissemination of useful knowledge, and be directly in line with their publication in past years, of the indexes to the literature of specific chemical bodies, which has so much redounded to their credit? It seems to me at least that it would be a work worthy of their best endeavor, and of whose great utility there could be no question whatever.

CAUSE OF THE LOSS IN WEIGHT OF COMMERCIAL PLATINUM, WHEN HEATED UNDER SOME CONDITIONS.

By Robert W. Hall.

Received June 15, 1900.

THE fact that commercial platinum sometimes loses weight when heated has been frequently noticed and experiments made to determine the cause of the loss. This loss has been observed under at least seven conditions.

1. *When platinum is made the cathode for the spark from an induction coil.*—That platinum is dissipated under this condition, was observed by Plücker[1] and very fully described by him. A. W. Wright[2] and others studied the same phenomena. The platinum is dissipated alike in air, in vacuum, and in hydrogen, and the phenomena are regarded as purely physical or mechanical.

2. *When platinum is heated in a Bunsen gas flame, sufficiently, reducing to deposit some carbonaceous matter on the platinum.*—Rémont[3] obtained in this way, in thirty minutes, a deposit weighing 22 milligrams and containing 10 milligrams of platinum. Rémont made some experiments to show that this loss is not due to the heated carbonaceous matter alone. He attributed it to some constituent of the gas.

3. *When platinum is heated in the ordinary smokeless Bunsen flame.*—Some observers note a constant loss under these conditions. Wittstein[4] found such a loss and attributes it to osmium, which he found in the platinum scrap of that time. Stolba[5] found that a platinum crucible lost weight at the rate of 16 milligrams in twelve hours. Stolba remarks that while he

1 *Ann. Phys. Chem.*, 103, 90 (1858).
2 *Sill. J. Sci. and Arts*, January, 1877.
3 *Bull. Soc. Chim.*, 35, 486 (1881).
4 Dingler's *poly. J.*, 179, 299 (1866).
5 *Ibid.*, 198, 177 (1870).

does not deny the possible presence of osmium, there would have to be more osmium in the platinum than in the original ore, to account for the continuous losses he observed. Erdmann,[1] with Pettenkofer, had, however, studied the behavior of platinum crucibles in the Bunsen flame and observed the formation of a gray coating, but without loss or gain in weight. Erdmann concludes that the gray coating is due to molecular change in the platinum. Crookes[2] discusses Erdmann's paper and agrees with him.

The writer's experience agrees with that of Erdmann, so far as constancy of weight is concerned. Possibly some of the platinum of commerce about 1866 to 1870 differed in composition from that commonly used. It may be noted here that platinum heated in a flame of hydrogen containing arsine and then strongly ignited, shows the phenomena observed by Erdmann in a very marked degree.

4. *When platinum is very strongly heated in a furnace for firing porcelain.*—Elsner[3] found that platinum burned into porcelain, was entirely dissipated when exposed to the full heat of an oven used for firing porcelain, during the burning of a batch.

Platinum black, however, placed in a small porcelain crucible, under the same conditions, only melted to small globules, with a metallic luster.

5. *When platinum is heated in a combustion tube in air.*—H. Kayser[4] attempted to free air from possible hydrocarbons by passing it over platinum in a glass tube heated externally. He observed phenomena, which he explained by the assumption that the platinum gave up finely divided particles to the air.

6. *When platinum is heated by an electric current.*—That platinum is dissipated when heated in air by the electric current seems to have been discovered first by Thomas A. Edison.[5]

Edison observed that glass, surrounding the wire, became covered with a mirror of what he assumed to be metallic platinum and that when the wire was placed in a bulb and as

[1] *J. prakt. Chem.*, 79, 117 (1860).
[2] "Select Methods in Chemical Analysis," 2nd Ed., p. 681.
[3] *J. prakt. Chem.*, 99, 257 (1866), from *Chem. tech. Mitth.* (Elsner) 7, 36 (1857-1858).
[4] *Ann. Phys. Chem.*, 34 (1888).
[5] *Chem. News*, 40. 152, from *Proc. Am. Ass.*, 1879, 173.

perfect a vacuum as possible produced, the loss ceased. Edison pronounced the action to be purely mechanical.

Nahrwold,[1] in apparent ignorance of Edison's work, repeated part of Edison's experiments and further observed that the metallic coating dissolved in aqua regia, only in part. Nahrwold pronounces no opinion as to the nature of the action.

Berliner[2] endeavored to explain the action. He found that platinum, which had been exposed to air, gave up gas when heated in a vacuum, that while doing so platinum was dissipated, giving a deposit on glass cylinders surrounding the metal and that the dissipation of the platinum ceased, when gas was no longer given off. In hydrogen the behavior was exactly the same as shown by a single successful experiment and Berliner, therefore, concluded that the action was a purely mechanical one caused by the escaping gases.

7. *When platinum is heated before the blast-lamp.*—Beilstein[3] notes that platinum crucibles, both of pure and of less pure platinum, lost weight to an important degree on ignition but that after repeated ignition the loss became less. The writer's experience does not agree with this. For example, in a series of experiments, a crucible which had been used for some years, was ignited nineteen times, under varying conditions, with a total loss of 10.3 milligrams; on being ignited for the twentieth time (see Table B, Experiment 1) it showed a loss of 2 milligrams in thirty minutes,—a greater loss than was observed in any of the preceding experiments. Perhaps if a new crucible had been used for the first experiment of the series, results like Beilstein's, would have been obtained.

The attention of the writer was directed to the subject soon after moving to a new laboratory, by finding that the ordinary platinum crucibles of commerce lost weight so rapidly, when used for the conversion of calcium oxalate into calcium oxide, that even an approximately constant weight could not be reached.

This was the more remarkable, as the burners and general arrangements were the same, as had been used for several years,

[1] *Ann. Phys. Chem.*, **31**, 467 (1887).

[2] *Ibid.*, **33**, 287 (1888).

[3] Short abstract *Chem. Centrbl.*, 1880, 614. Original in *Z. rusk. chim. obse.*, **12**, 1880, not accessible.

with the exception that for a foot-blower, there was substituted a steady blast from a blowing engine, giving a more evenly high temperature.

The gas used was a mixture of retort gas and of the so-called "water-gas" enriched with naphtha gas. It contained about 15 per cent. of carbon monoxide and in this respect resembled the gas, which had been used formerly, without causing any loss of weight in the crucibles.

The loss was not due to the high temperature alone, for the writer has frequently heated crucibles with a steady blast, to the most brilliant "blue whiteness," without loss.

Experiments showed that the loss was not due to dust in the air or gas, acting as a sand-blast, for filtration of the air and gas through cotton-wool made no difference; nor to unusual amounts of the impurities removable by alkalies in the gas, for the losses still continued after a careful purification of the gas by passing it through potassium hydroxide solution and over "soda-lime."

Nor was the loss likely to be due to any peculiarity in the platinum used, for old and new crucibles of soft, comparatively pure platinum and a crucible of a platinum-iridium alloy, gave about the same results. In every case, after heating, the platinum showed a somewhat roughened surface, with a most beautiful silvery luster.

TABLE A.

Soft, commercial "pure" platinum from Eimer and Amend, New York.

No.	Weight of wire before heating.	Weight after heating.	Gas used.	Duration of experiment in minutes.	Loss or gain in milligrams.	Loss per 15 minutes.	Remarks.
1.	2.9085	2.9085	CO	30	0.0	0.00	
2.	2.9085	2.9085	"	30	0.0	0.00	
3.	2.9083	2.9080	"	35	—0.3	0.13	Supply of gas insufficient. Some air may have gained access.
4.	2.9080	2.9054	air	30	—2.6	1.30	Slight mirror on the glass.
5.	2.9054	2.9022	"	30	—3.2	1.60	Slight mirror on the glass.
6.	2.9022	2.8977	"	45	—4.5	1.50	Slight mirror on the glass.

No.	Weight of wire before heating.	Weight after heating.	Gas used.	Duration of experiment in minutes.	Loss or gain in milligrams.	Loss per 15 minutes.	Remarks.
7.	2.8977	2.8889	air	90	—8.8	1.46	Slight mirror on the glass.
8.	1.7258	1.7137	"	60	—12.1	3.02	Mirror. Thinner wire. Higher resistance. Current more easily regulated. Hence heat higher.
9.	1.7137	1.6905	oxygen	60	—23.2	5.80	
10.	1.6905	1.6902	CO_2	90	—0.3	0.05	
11.	2.8889	2.8716	oxygen	85	—17.3	3.05	Mirror. Heat not high. Difficult to regulate current owing to small resistance.
12.	2.8468	2.7165	"	360	—130.3	5.43	Glass covered with an almost opaque mirror.
13.	3.0935	3.0939	hydrogen	60	+0.4		Hydrogen found to contain some arsine.
14.	2.8714	2.8715	"	90	+0.1		Hydrogen free from arsine.

Some experiments were therefore undertaken to answer the question why platinum crucibles sometimes keep a constant weight, when heated in a gas flame, to a temperature very near their melting-point and why they sometimes lose weight, at a rate amounting to a milligram in fifteen minutes.

Wires of the ordinary soft "pure" platinum of commerce, about 40 cm. in length, were placed within a glass tube 78 cm. in length and 3.5 cm. in diameter, closed at each end with caoutchouc stoppers and provided with openings for the introduction and exit of the different gases used.

The platinum wires used were hung on platinum rods and these again hung on copper conducting wires. A stream of the gas used was passed through the apparatus and then the wire was brought to a temperature as near its melting-point as could be done safely, by means of an electric current.

The details of these experiments are given in table A.

The results of these experiments was unexpected.

They show that the loss of weight, in the reducing or neutral gases, carbon monoxide or carbon dioxide, is zero or very slight; that in hydrogen there is a very slight gain, while

in air and oxygen the loss is very rapid, in Experiment No. 12, amounting to 5.4 milligrams in each fifteen minutes. The two experiments with hydrogen, showing an actual gain, are not necessarily in conflict with Berliner's result, since in these two experiments the platinum was cooled in hydrogen, while in Berliner's experiment the platinum was cooled in a vacuum. The following experiments were made, however, and do seem to conflict with Berliner's result. The wires used in Experiments 13 and 14, were heated by the current, for sixty and ninety minutes, respectively, in an atmosphere of carbon dioxide. After this treatment they weighed within 0.05 milligram of the original weights; that is, the differences were within the error of weighing. It may be remarked that Berliner's experiments were qualitative, but he describes the deposit from hydrogen as an "opaque platinum mirror." Berliner's experiments were beautifully planned and no explanation of the apparent conflict suggests itself.

It, therefore, appeared probable from the result of these experiments, that a highly oxidizing gas flame would cause a greater loss of platinum, than a more reducing one.

Experiments were made to test this by placing a platinum crucible in a blast-flame, first high up in the flame, above the point where the maximum temperature could be reached and where the flame should be oxidizing and then bringing it down by steps, nearer the burner, below the zone of maximum temperature, where the flame should be more reducing, under the following conditions.

Two burners, with converging flames were used, a steady blast from a blowing engine, the flame surrounded by perforated clay crucibles, the blast adjusted in each case so as to give the maximum heat, in the particular position; duration of each experiment thirty minutes.

Weight of the platinum crucible, 11.9694 grams.

The following results were obtained:

TABLE B.

No. of Exp.	Distance between bottom of crucible and the burners. cm.	Loss of weight. Mgs.	Loss per 15 minutes. Mgs.	Remarks.
1.	15.5	2.0	1.0	Heat below that of four succeeding experiments.
2.	12.5	1.1	0.55	Good white heat.
3.	10.5	0.8	0.40	Heat higher than in No. 2.
4.	8.5	0.5	0.25	
5.	7.5	0.5	0.25	Heat as high as in No. 3.
6.	6.5	0.5	0.25	Heat lower than in No. 5. Seemed about the same as in No. 1.

In these experiments the loss in weight varied so much more with the position in the flame, than with the temperature, that the latter relation is entirely masked.

In all cases, where the wires lost weight, when heated by electricity in air or oxygen, mirrors were produced on the glass tube.

In Experiment No. 12, table A, the deposit was removed by aqua regia; only part of it dissolved at first in concentrated aqua regia, just as Nahrwold observed. The solution was filtered from the insoluble part, precipitated by ammonium chloride, and the precipitate ignited. The residue weighed 56.3 milligrams. The insoluble portion was ignited and found to weigh 56.4 milligrams. After ignition this residue dissolved in concentrated aqua regia. A further black precipitate was obtained from the alcoholic filtrate from the precipitation of the first aqua regia solution, which weighed 1.3 milligrams. Hence, if it is assumed that the mirror and these three fractions had about the same composition there were recovered in all 114 milligrams out of 130.3 milligrams. Some of the deposit lay on the platinum supports and could not be recovered.

The behavior of the aqua regia solutions was very different from that of 130 milligrams of the original wire.

These experiments show that the loss of weight of commercial platinum heated by the electric current or before the blast-lamp, is due to the chemical action of oxygen, that certain elements are fractioned out of the impure platinum and that the loss of weight is not, as has been suspected, due to the use of "water-

gas'', except in so far as this gas is likely to give a hot and strongly oxidizing flame, when used in burners having an air supply, designed for a gas requiring more oxygen.

The behavior of platinum when heated under the last five conditions may be explained by the hypothesis that a volatile oxide of platinum is formed, stable at high and low temperatures, but unstable at intermediate temperatures, like the platinous chloride ($PtCl_2$) of Troost and Hautefeuille.[1]

If, as is the case in the blast-flame, the compound is swept away or if, as in the porcelain furnace in the combustion tube and with the heated wire, there is no cooler part of the platinum, upon which the metallic product of the decomposition of the hypothetical oxide can settle, the platinum loses weight. If on the contrary the flame is a quiet one, as is the case when a crucible is heated in a Bunsen flame, and only a part of the metal is very strongly heated, the hypothetical oxide decomposes at once on emerging from the most strongly heated zone and the platinum is deposited on the cooler part of the crucible, producing the molecular change of the surface, without gain or loss of weight, noticed by Erdmann and Crookes.

It is hoped to continue this work in this laboratory, to examine the deposit, to test the behavior of purer platinum, to try to isolate the hypothetical oxide and to fix, if possible, the conditions under which commercial platinum may be heated to whiteness without loss.

LABORATORY OF ANALYTICAL CHEMISTRY,
HAVEMEYER CHEMICAL LABORATORY,
NEW YORK UNIVERSITY, June, 1900.

THE PRECIPITATION OF THE SULPHIDES OF NICKEL AND COBALT IN AN ALKALINE TARTRATE SOLUTION, TOGETHER WITH AN INVESTIGATION INTO THE NATURE OF CERTAIN TARTRATES OF THESE METALS.

BY O. F. TOWER.

Received June 19, 1900.

INTRODUCTION.

VILLIERS[2] recommended some time ago a method for the qualitative separation of nickel and cobalt based on the action of hydrogen sulphide on an alkaline solution of the tartrates

[1] *Compt. rend.*, **84**, 946 (1877).
[2] *Ibid.*, **119**, 1263, and **120**, 46 (1894-95).

TABLE B.

No. of Exp.	Distance between bottom of crucible and the burners. cm.	Loss of weight. Mgs.	Loss per 15 minutes. Mgs.	Remarks.
1.	15.5	2.0	1.0	Heat below that of four succeeding experiments.
2.	12.5	1.1	0.55	Good white heat.
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5.	7.5	0.5	0.25	Heat as high as in No. 3.
6.	6.5	0.5	0.25	Heat lower than in No. 5. Seemed about the same as in No. 1.

In these experiments the loss in weight varied so much more with the position in the flame, than with the temperature, that the latter relation is entirely masked.

In all cases, where the wires lost weight, when heated by electricity in air or oxygen, mirrors were produced on the glass tube.

In Experiment No. 12, table A, the deposit was removed by aqua regia; only part of it dissolved at first in concentrated aqua regia, just as Nahrwold observed. The solution was filtered from the insoluble part, precipitated by ammonium chloride, and the precipitate ignited. The residue weighed 56.3 milligrams. The insoluble portion was ignited and found to weigh 56.4 milligrams. After ignition this residue dissolved in concentrated aqua regia. A further black precipitate was obtained from the alcoholic filtrate from the precipitation of the first aqua regia solution, which weighed 1.3 milligrams. Hence, if it is assumed that the mirror and these three fractions had about the same composition there were recovered in all 114 milligrams out of 130.3 milligrams. Some of the deposit lay on the platinum supports and could not be recovered.

The behavior of the aqua regia solutions was very different from that of 130 milligrams of the original wire.

These experiments show that the loss of weight of commercial platinum heated by the electric current or before the blast-lamp, is due to the chemical action of oxygen, that certain elements are fractioned out of the impure platinum and that the loss of weight is not, as has been suspected, due to the use of "water-

gas'', except in so far as this gas is likely to give a hot and strongly oxidizing flame, when used in burners having an air supply, designed for a gas requiring more oxygen.

The behavior of platinum when heated under the last five conditions may be explained by the hypothesis that a volatile oxide of platinum is formed, stable at high and low temperatures, but unstable at intermediate temperatures, like the platinous chloride ($PtCl_2$) of Troost and Hautefeuille.[1]

If, as is the case in the blast-flame, the compound is swept away or if, as in the porcelain furnace in the combustion tube and with the heated wire, there is no cooler part of the platinum, upon which the metallic product of the decomposition of the hypothetical oxide can settle, the platinum loses weight. If on the contrary the flame is a quiet one, as is the case when a crucible is heated in a Bunsen flame, and only a part of the metal is very strongly heated, the hypothetical oxide decomposes at once on emerging from the most strongly heated zone and the platinum is deposited on the cooler part of the crucible, producing the molecular change of the surface, without gain or loss of weight, noticed by Erdmann and Crookes.

It is hoped to continue this work in this laboratory, to examine the deposit, to test the behavior of purer platinum, to try to isolate the hypothetical oxide and to fix, if possible, the conditions under which commercial platinum may be heated to whiteness without loss.

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NEW YORK UNIVERSITY, June, 1900.

THE PRECIPITATION OF THE SULPHIDES OF NICKEL AND COBALT IN AN ALKALINE TARTRATE SOLUTION, TOGETHER WITH AN INVESTIGATION INTO THE NATURE OF CERTAIN TARTRATES OF THESE METALS.

BY O. F. TOWER.

Received June 19, 1900.

INTRODUCTION.

VILLIERS[2] recommended some time ago a method for the qualitative separation of nickel and cobalt based on the action of hydrogen sulphide on an alkaline solution of the tartrates

[1] *Compt. rend.*, **84**, 946 (1877).
[2] *Ibid.*, **119**, 1263, and **120**, 46 (1894-95).

of these metals. This method as commonly carried out may be stated as follows: The solution of the sulphides of nickel and cobalt in aqua regia is evaporated to expel chlorine, and after suitable dilution sufficient tartaric acid is added to prevent precipitation by sodium hydroxide. This last reagent is then added until the solution is strongly alkaline, and hydrogen sulphide run in to saturation. Cobalt sulphide is precipitated, while nickel sulphide remains in solution, imparting to the solution a dark color. When nickel is present only in very small quantities the color is brown; with larger quantities it is a jet black.

The failure of this method to give good results in the hands of students, has led to a critical investigation of it, the results of which are given in the following pages. In order to be able to approach this subject intelligently this account will be preceded by an account of an investigation into the nature of some tartrate solutions of nickel and cobalt, together with a description of any such tartrates which it has been found possible to isolate.

All substances before being analyzed were dried in an air-bath at 120°.

Nickel and cobalt were always determined electrolytically following in most respects the method of Fresenius and Bergmann,[1] which may be outlined as follows: To the solution containing nickel or cobalt, which is free from chlorides, are added 100 cc. ammonia solution (sp. gr. 0.96) and 10 cc. of a solution of ammonium sulphate (305 grams to liter). A current from two storage battery cells (3.2 volts, 0.48 ampere) was passed through the solution for from four to five hours. This length of time was found to be sufficient to effect complete precipitation of the metal (quantities not exceeding 0.1100 gram), provided tartrates were absent. It was necessary, however, to determine these metals frequently in the presence of tartrates. In such cases the amount of metal deposited at the end of four or five hours was weighed, removed from the electrode, and the apparatus then reconnected and left running all night. The results were then very satisfactory.

Potassium was determined as sulphate. After removing the nickel either by precipitation as sulphide or by electrolysis, tar-

[1] *Ztschr. anal. Chem.*, 19, 314 (1880).

taric acid was destroyed by gentle ignition, and the potassium then converted into sulphate by heating with ammonium sulphate.

TARTRATES OF NICKEL.

The effect of tartaric acid in preventing the precipitation of the hydroxides of nickel and cobalt has been known since the time of Rose,[1] and since then has been frequently discussed. The literature on the preparation of well-defined tartrates of these metals is, however, rather meagre.

That nickel tartrate cannot be precipitated from solutions of nickel salts is well known. Werther[2] prepared it by saturating a boiling solution of tartaric acid with freshly precipitated nickel hydroxide. The substance was thrown down as a pale green powder practically insoluble in hot or cold water, but soluble in warm alkalies. This has been essentially confirmed. The precipitate is apparently amorphous, although Werther considered it crystalline. The filtrate is still colored green, showing that precipitation is incomplete, but what is precipitated is extremely insoluble in water. The substance washed and dried at 120° yielded 28.44 per cent. nickel. The theoretical percentage of nickel in $NiC_4H_4O_6$ is 28.39. This substance dissolves readily in alkalies, only when they are present in large excess. To effect solution, considerably more potassium hydroxide is required than a quantity equivalent to the nickel tartrate; that is, more than two molecules potassium hydroxide to one nickel tartrate, and the action is greatly accelerated by heating. The behavior of this nickel tartrate toward atmospheric moisture is worthy of remark. The precipitated powder dried at 50° still contains moisture. In this condition, however, it neither deliquesces nor effloresces, the moisture content remaining constant. On the other hand no definite hydrate seems to exist, for different samples on drying at 120° were found to contain different percentages of residual water. Furthermore, the water-free substance is not in the least hygroscopic. When exposed under a bell-jar to an atmosphere saturated with moisture, it does not gain in weight more than a milligram or two in several weeks. Nickel tartrate can be made

[1] Gilbert's *Annalen*, **73**, 74, foot-note (1823).
[2] *J. prakt. Chem.*, **32**, 400 (1844).

equally well by treating a hot solution of tartaric acid with nickel carbonate.

Fresenius[1] prepared a hydrated racemate of nickel from nickel acetate and racemic acid. It resembles nickel tartrate in some of its characteristics but was not further investigated.

If freshly precipitated nickel hydroxide is treated with cold dilute tartaric acid, the nickel hydroxide dissolves, imparting to the solution a green color, probably due to the formation of nickel tartrate. On warming this solution the light green powder mentioned above precipitates. To determine the molecular size of the substance in solution, a solution was prepared by treating an excess of nickel hydroxide with a known quantity of tartaric acid, and then finding the freezing-point of the resulting solution. The reaction between nickel hydroxide and tartaric acid is very slow, so that after five days' standing free tartaric acid was still present in sufficient quantity to redden blue litmus paper, 2 or 3 milligrams of the acid being uncombined. This was not sufficient to influence materially the results which follow. The apparatus employed for the freezing-point determinations was Beckmann's improved form,[2] and is particularly designed to exclude moisture from the solution during the process. This is accomplished by operating the stirrer by means of an electromagnet, thereby obviating the necessity of having a hole through the stopper for the stirring shaft. Since aqueous solutions were used in these experiments, the exclusion of moisture made very little difference, but this form of apparatus has other advantages. It is exceedingly convenient, requiring the operator's attention only for a few minutes at the time of freezing, and besides the regularity of stirring insures greater accuracy. Individual determinations of the freezing-point of the same substance did not vary more than 0.002°. Five cells of a storage battery were used to supply power for the electromagnet. Table 1 gives the results with solutions of nickel tartrate prepared as indicated above. The last four are with different concentrations of the same solution. The strength of such solutions was always determined by precipitating the nickel in an aliquot portion by electrolysis.

[1] *Ann. Chem.* (Liebig), **41**, 23 (1842).
[2] *Ztschr. phys. Chem.*, **21**, 239 (1896).

TABLE 1.

Amount $NiC_4H_4O_6$ in 100 cc. solution. Grams.	Depression.	Apparent Molecular weight.
1.8795	0.139°	260
1.7205	0.121°	273
0.8602	0.081°	202
0.4301	0.042°	193
0.2150	0.025°	163

Molecular weight of $NiC_4H_4O_6 = 206.8$.

In the case of the more concentrated solutions these results show the molecular weight calculated from the lowering of the freezing-point to be higher than that calculated from the formula. One would expect, however, the reverse, because of dissociation in aqueous solution. By the freezing-point method Kahlenberg has shown the apparent molecular weight of potassium tartrate in solutions of moderate strength to be about one-half that calculated from the formula, $K_2C_4H_4O_6$.[1] These facts lead to the conclusion that nickel tartrate exists in fairly concentrated solutions largely in the form of double molecules.

Determinations of the electrical conductivity of these solutions show abnormal results also. In Table 2, m is the fraction of a gram-equivalent ($\frac{1}{2}NiC_4H_4O_6$) in a liter; L, is the equivalent conductivity expressed in reciprocal ohms.[2]

TABLE 2.

Temperature 18°. Nickel tartrate.		Temperature 25°. Magnesium tartrate.[3]	
m.	L.	m.	L.
0.1664	8.29	0.03125	54.9
0.0832	9.34	0.0156	64.1
0.0416	10.8	0.0078	74.0
0.0208	18.7	0.0039	82.6
0.0104	26.5	0.0020	90.1
0.0052	36.8	0.0010	95.9
0.0026	48.8	.....	....
0.0013	63.6	.....	....

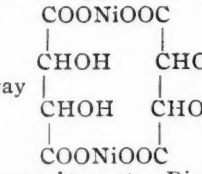
The values of the conductivity of nickel tartrate are exceptionally small, as will be seen by comparing them with the values for magnesium tartrate, which illustrate normal conduc-

[1] *Ztschr. phys. Chem.*, 17, 585 (1895).

[2] These units are those proposed by Kohlrausch, and fully described in "Leitvermogen der Elektrolyte," by Kohlrausch and Holborn.

[3] Determinations by Walden, *Ztschr. phys. Chem.*, 1, 537 (1887), recalculated by Kohlrausch and Holborn.

tivities of tartrates of this class. The different behavior of nickel tartrate can only be ascribed to a peculiar constitution of the salt itself. In seems reasonable to suppose that a substance with the atoms arranged in this way



might well suffer less dissociation than a normal tartrate. Dissociation in concentrated solutions would probably be of the nature, $\overset{+}{Ni}\overset{+}{\cdot}$ and $\overset{-}{C_4H_4O_6}\overset{-}{NiC_4H_4O_6}$. On dilution this anion itself would gradually be decomposed, so that the conductivity would not advance with the same regularity as it does in the case of simple binary electrolytes. In Table 2, the results with nickel tartrate show such behavior, as is seen by comparison with the value for magnesium tartrate. Such a formula as the above will also explain very satisfactorily the results obtained from the freezing-point method. Measurements of the electromotive forces with solutions of this kind will not be given, until the facts relating to some other tartrates of nickel have been discussed.

Fabian[1] prepared potassium nickel tartrate by allowing cream of tartar to act on nickel carbonate at a temperature of about 50°. On evaporating the solution obtained over sulphuric acid a greenish substance was deposited, which effloresced on exposure to air and was soluble in water. After drying this substance at 110° and analyzing, he obtained the following results:

	Found. Per cent.	Theory for $NiK_2C_8H_8O_{12}$. Per cent.
NiO	16.8	17.3
K_2O	20.9	21.7

This work has been repeated with essentially the same results. Cream of tartar was allowed to stand in contact with an excess of nickel carbonate at about 40° for some time. The green solution was filtered off, and left to evaporate over sulphuric acid. No definite crystals were obtained, neither by evaporating rapidly in a partial vacuum nor slowly in the air with a string. The residue was invariably of a scaly appearance possessing

[1] *Ann. Chem.* (Liebig), 103, 248 (1857).

a very light green color. The results of the analysis of this substance are:

	Found. Per cent.	Theory for $K_2NiC_8H_8O_{12}$. Per cent.
K	18.21	18.06
Ni	13.38	13.55

According to Fabian, on boiling a solution of this substance a gelatinous mass separates out, which cannot be washed completely free from alkali. This has been found to be true, the precipitate being rather flocculent and of a very light green color. If, however, a solution of potassium nickel tartrate is digested for some time at about 75°, a light green pulverulent precipitate can be obtained, which was supposed to be a basic tartrate of nickel. After washing it thoroughly and drying at 120°, analysis proved it to be identical with the insoluble nickel tartrate already described, a sample yielding 28.25 per cent. nickel. On long standing this decomposition takes place gradually at lower temperatures. It is, therefore, necessary to exercise care in the preparation of potassium nickel tartrate, for, if tartaric acid is digested for a long time with nickel carbonate, some of the potassium nickel tartrate formed is apt to decompose in this manner:

$$K_2NiC_8H_8O_{12} = \underset{\text{Insoluble form}}{NiC_4H_4O_6} + K_2C_4H_4O_6.$$

When the solution is filtered, the potassium tartrate passes through with the potassium nickel tartrate, and remains mixed with it on evaporation. This is revealed by the percentage of potassium being too high and that of nickel too low to correspond to the formula $K_2NiC_8H_8O_{12}$.

Determinations of the molecular weight of this substance were made by means of the freezing-point method. For this purpose different solutions were employed,—some prepared as above described, some by dissolving the solid substance in water, and others by dissolving nickel hydroxide in the proper amount of tartaric acid and adding that quantity of potassium hydroxide just sufficient to form $K_2NiC_8H_8O_{12}$. The results follow:

TABLE 3.

	Amount $K_2NiC_8H_8O_{12}$ in 100 cc. solution. Grams.	Depression.	Apparent molecular weight.
Solution prepared direct from $NiCO_3$ and $HKC_4H_4O_6$	3.764	0.434°	162
	1.882	0.255	140
	0.941	0.170	105
Solid substance dissolved in water.....	3.752	0.430	165
	1.876	0.253	140
Solution prepared from $Ni(OH)_2$, $H_2C_4H_4O_6$ and KOH.....	3.295	0.419	153
	1.6475	0.246	128
	0.8238	0.139	112
	0.4119	0.079	98

Molecular weight of $K_2NiC_8H_8O_{12} = 433$.

It is essential to know something about the dissociation of this substance before one can judge intelligently of its true molecular size. To throw light on this subject the electrical conductivity of a solution of potassium nickel tartrate was measured. The equivalent conductivity is given on the basis of one potassium atom ($\frac{1}{2}$ molecule $K_2NiC_8H_8O_{12}$ in a liter).

TABLE 4.

Temperature 18°. Potassium nickel tartrate.		Temperature 25°. Sodium tartrate.[1]	
m.	L.	*m.*	L.
0.1522	74.6	.....	.....
0.0761	84.3	.....	.....
0.0381	94.2	0.03125	87.1
0.0190	101	0.0156	93.2
0.0095	114	0.0078	98.2
0.0048	124	0.0039	102.1

The conductivity of the double tartrate is increasing with the dilution much faster than that of the sodium tartrate. This is undoubtedly due to the dissociation of potassium nickel tartrate mostly into $\overset{+}{K}$ ions and $\overline{NiC_8H_8O_{12}}$ ions in the more concentrated solutions. On dilution, however, the nickel also begins to dissociate from the complex anion, thus causing the rapid increase in the conductivity. For corresponding concentrations the conductivity of the double tartrate always exceeds that of the sodium tartrate.

Kahlenberg,[2] in his article on complex tartrates of lead and

[1] The conductivity of sodium tartrate is given for comparison. The results are those of Bredig, *Ztschr. phys. Chem.*, **13**, 191 (1894), recalculated by Kohlrausch and Holborn.

[2] *Ztschr. phys. Chem.*, **17**, 577 (1895).

copper, found that these substances were probably dissociated sufficiently, so that the apparent molecular weight was about one half the true molecular weight. The solutions of potassium nickel tartrate used here were, however, a little more dilute than Kahlenberg's solutions ; besides the substances are somewhat different in nature. Table 3 shows the apparent molecular weight to be only a little more than $\frac{1}{3}$ of the molecular weight of $K_2NiC_8H_8O_{12}$. This may be accounted for on two hypotheses ; either the substance is in large part dissociated into $\overset{+}{K}$, $\overset{+}{K}$ and $Ni\overset{=}{C}_8H_8O_{12}$ ions as was indicated in connection with the conductivity measurements, or there exist separately in the solution potassium tartrate and nickel tartrate, the former dissociated, the latter, however, not. The evidence seems to favor the former of these hypotheses. For, if the second were correct, one would expect the deposit left on evaporation of the solution not to have a uniform composition. But the deposit on the side of the dish was of the same composition as that on the bottom. Furthermore, washing the deposit slightly with water had no effect on its composition. If the substance had been a mixture of potassium tartrate and nickel tartrate, this treatment would very likely dissolve more of the former salt than of the latter.

The fact that the addition of tartaric acid to solutions of nickel salts prevents the precipitation of nickel hydroxide is usually explained by the supposition that in such cases the nickel replaces the hydrogen atoms of the alcoholic hydroxyls of the tartaric acid, while the potassium takes the place of the two carboxyl hydrogen atoms. The formula of such a substance would be $\begin{matrix} COOK \\ | \\ CHO \\ | \\ CHO \\ | \\ COOK \end{matrix} > Ni$. To see if any experimental basis can be found for this view, solutions of nickel tartrate, to which potassium hydroxide had been added, were investigated by the usual physico-chemical methods.

The freezing-point method was first employed in order to observe the effect on the size of the molecule of successive

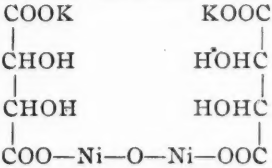
additions of potassium hydroxide[1] to a solution of nickel tartrate.

TABLE 5.

Solution containing 1.8795 grams nickel tartrate in 100 cc.

Expt. No.	KOH added to above solution. Gram.	Depression.	Remarks.
1	0.0000	0.139°	Reaction acid.
2	0.1226	0.180	Reaction alkaline.
3	0.3270	0.187	
4	0.5314	0.134	
5	0.7358	0.180	Solution jelly-like.
6	0.8175	0.156	
7	1.311	0.233	

In Experiment 7, the quantity of potassium hydroxide is just sufficient to form, with the nickel tartrate, $K_2NiC_4H_2O_6$. In the fourth the depression is a minimum, and here the amount of potassium hydroxide added is nearly one half that added in the seventh, or the ratio is about one molecule potassium hydroxide to one nickel tartrate. If the molecular weight is calculated from the depression, 0.134°, on the basis of $NiKC_4H_3O_6$ existing in solution, 299 is obtained. The molecular weight according to the above formula is in round numbers 245. This case is almost exactly parallel to the results obtained by Kahlenberg[2] with certain alkaline tartrate solutions of lead and copper. So undoubtedly the molecular size of the substance here is about twice that represented by the formula $NiKC_4H_3O_6$, and following Kahlenberg the molecular structure may be represented as follows:



Such a substance would hardly be expected to dissociate so as to yield nickel ions. The evidence for such a molecular structure would, therefore, be increased, if it could be shown that no nickel ions exist in the solution.

For this purpose measurements were made of the electromotive force generated by an element with nickel electrodes, one

[1] Sodium hydroxide was also employed, but since the results are similar, only those with potassium hydroxide are given.

[2] *Loc. cit.*

electrode being surrounded by a solution of a nickel salt of known concentration and the other surrounded by the solution in question. The electromotive force of such an element is expressed by the formula,

$$\pi = \frac{RT}{nE_0} ln \frac{c_1}{c_2} ,$$

where the letters indicate the usual quantities, c_1 and c_2 being the concentration of the nickel ions in the two solutions. Evaluating the equation for R = 8.311 electrical units, T = 291 (18° C.), n, the valence of nickel = 2, E_0 = 96,540 coulombs, and reducing to Briggs' system of logarithms, one obtains,

$$\pi = 0.02881 \log \frac{c_1}{c_2} .$$

Measurements were made according to the Poggendorf-Ostwald method with a Lippmann capillary electrometer. The nickel solution of constant concentration was in every case a solution of nickel nitrate containing 0.1 gram-molecule in a liter. The electrodes were made by covering platinum electrodes with nickel by electrolysis. These electrodes were tested by connecting them with an electrometer, when they were dipping into the same solution of nickel nitrate. Under these conditions the electrometer reading should be zero. Few electrodes, however, could be found which would fulfil this condition. Those chosen showed potential differences of not more than 0.003 volt. Measurements were made first of the electromotive forces between the standard solution and solutions of nickel nitrate containing 0.05 and 0.01 gram-molecule in a liter, respectively, and afterwards with the solutions of nickel tartrate under consideration. In each case the electrodes were reversed and the potential difference measured again. The averages of the two readings so obtained are given in Table 6.

TABLE 6.

Temperature 18°.

No.	Between 0.1 mol. $Ni(NO_3)_2$ and	E observed. Volt.	E calculated. Volt.
1	0.05 mol. $Ni(NO_3)_2$	0.010	0.0087
2	0.01 " "	0.032	0.0288
3	0.0208 " $(NiC_4H_4O_6)_2$	0.048	.....
4	0.0761 " $NiK_2C_8H_8O_{12}$	0.075	.....
5	0.0572 " $KC_4H_4O_6NiONiO_6H_4C_4K_2$	0.210	.....
6	0.0748 " $K_2NiC_4H_2O_6$	0.236	.....

Where the concentration of the nickel ions was known the electromotive force has been calculated from the formula. The agreement is seen to be fairly good. Nos. 3 and 4 are measurements with the solutions already mentioned of nickel tartrate and potassium nickel tartrate, respectively. The potential differences show that the concentration of the nickel ions in these solutions is somewhat less than in a 0.01 mol. solution of nickel nitrate. Fewer nickel ions are present in the potassium nickel tartrate solution than in the solution of nickel tartrate, which was to be expected, for the same reason that the replaceable hydrogen atom of an acid salt is only very slightly dissociated.[1]

To find the concentration of the nickel ions in solution 5, which is the one formed by adding to 100 cc. of a solution containing 18.795 grams of nickel tartrate, 0.5314 gram of potassium hydroxide,[2] 0.210 is substituted for π in the formula and c_1 is made equal to 0.1×0.8, for 0.1 mol. nickel nitrate is about 80 per cent. dissociated. From this the value of c_2 is found to be $10^{-8.386}$. This shows that, relatively speaking, no nickel ions are in the solution, which is corroborative evidence of the existence of the molecular structure ascribed to this substance on page 510.

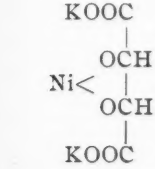
Referring to Table 5, it will be noticed that the depression gradually increases with the addition of potassium hydroxide from the fourth experiment to the seventh, except in No. 5. In this case the contents of the tube were viscous having the consistency of thin jelly, which interfered materially with the determination. This gelatinous mass completely dissolved on addition of more potassium hydroxide. The appearance of this substance is peculiar. The green liquid simply solidifies to a transparent mass without any change in appearance. On reversing the tube containing the substance it is found to be solid or viscous according to the amount of water present, and this is the only evidence of a change. On standing for a length of time it gradually becomes opaque. Several years ago this phenomenon was observed by Professor Bradley, of Middletown, who called my attention to it at that time. He obtained it by adding first tartaric acid to a solution of nickel sulphate and then adding a solution of potassium hydroxide drop by drop

[1] For the discussion of this, see Ostwald: *Ztschr. phys. Chem.*, 9, 553 (1892).

[2] See Table 5.

until the mass gelatinized. As can be seen from Table 5, it is formed when about one molecule of nickel tartrate is treated with one molecule of potassium hydroxide. It was shown just before the solution gelatinized (experiment 4, Table 5), that from the depression of the freezing-point and other considerations the molecule probably is $KC_4H_4O_6NiONiO_6H_4C_4K$. It is, therefore, possible that this gelatinous mass is a hydrated form of that substance. Heating almost to the boiling-point completely dissolves it.[1]

To return to the effect on the depression of the freezing-point of adding potassium hydroxide, as seen in Table 5 from Experiment 4 on. Leaving out of consideration No. 5, where the solution was viscous, the increase in the depression from 0.134° to 0.156° and in the last case to 0.233° is by no means sufficient to be equal to the entire effect of the potassium hydroxide added, if it existed as such in the solution. 0.4935 gram more of potassium hydroxide was added in Experiment No. 7 than in No. 6. This quantity of potassium hydroxide should give normally a depression of 0.121°,[2] but the difference between 0.233° and 0.156° is only 0.077°. In No. 7 the proportion of potassium hydroxide to nickel tartrate is two molecules of the former to one of the latter, or in the proper ratio to form



, the molecular weight of which is 283. The apparent

[1] Since writing this, Prof. Bradley has kindly allowed me to look over an unpublished manuscript by himself and F. A. Johnston on "A Tartrate of Sodium and Nickel," which treats of the formation, conduct, and gives some results of the analysis of this gelatinous substance. It was prepared from nickel sulphate, tartaric acid, and sodium hydroxide. It was isolated by stirring it up in alcohol, filtering and then washing with an equal volume of alcohol and water. When so treated the gelatine frequently remains transparent for a long time. It was found difficult to dry it to constant weight over sulphuric acid, for it is exceedingly hygroscopic. Preliminary analysis of the substance after drying over sulphuric acid showed: water, 7.04 per cent.; sodium, 6.30 per cent.; nickel, 21.04 per cent. We obtain by calculation from the above formula plus 2 molecules of water, $Na_2Ni_2C_8H_8O_{13} + 2H_2O$: water, 7.04 per cent.; sodium, 9.00 per cent.; nickel, 23.95 per cent. The most marked difference between these results and the results of the analysis is in the percentage of sodium. This may be accounted for from the fact that the gelatine is strongly alkaline and that washing removes some of this alkali, so that the residue may not have a constant composition. However, it is not asserted that the above formula represents the composition of the substance, for more analyses are needed in which the amount of tartaric acid is also determined, before the differences in the above results are explained and a suitable formula established.

[2] Calculated from the constant for potassium hydroxide reported by Raoult, *Ann. chim. phys.* (5), **28**, 137 (1883).

molecular weight calculated from the depression, 0.233 is 185, which is a little more than half that calculated from the formula. Since such a substance would probably be dissociated in aqueous solution about as much as potassium tartrate,[1] it is very likely that a substance of the above formula does really exist in the solution. Nickel ions would not be expected to be present in any quantity in a solution of such a substance. The potential difference found between this solution and 0.1 mol. nickel nitrate is 0.256 volt (No. 6, Table 6). This shows that the concentration of the nickel ions is even less than in the preceding solution (No. 5), where the concentration of these ions was found to be $10^{-8.386}$. What has, therefore, probably taken place on the addition of potassium hydroxide from solution 4 to solution 7, Table 5, is that, although the potassium hydroxide is continually being removed from the field of action as such, the molecular structure of the substance in solution is undergoing a change; that is, the complex molecule, $KC_4H_4O_6NiONiO_6H_4C_4K$, is breaking up into the smaller molecule, $K_2NiC_4H_2O_6$; the number of molecules is, consequently, on the whole increased, and the depression of the freezing-point becomes greater.

TARTRATES OF COBALT.

Very little literature of a definite nature could be found on this subject. A tartrate of cobalt and a double tartrate of potassium and cobalt are mentioned in the following dictionaries of chemistry: Fehling's, Vol. 9 (1864); Watts', Vol. 5 (1868); Wurtz's, Vol. 3 (1878). Nearly all the early journals and such periodicals as Berzelius' *Jahresbericht*, Liebig and Kopp's *Jahresbericht*, the *Pharmaceutisches Centralblatt*, &c., were thoroughly searched, but no reference was found to the original articles describing these salts. Such works as Ladenburg's Dictionary, edition 1894, and Beilstein's, third edition, mention no such substances. It is, therefore, to be inferred that the original article contained nothing very definite. Fresenius[2] prepared certain racemates of cobalt, but gives no analyses.

Cobalt tartrate can be made in the same manner as nickel tartrate, by saturating hot tartaric acid with cobalt hydroxide

[1] See Kahlenberg, *loc. cit.*

[2] *Ann. Chem.* (Liebig), 41, 22 (1842).

or carbonate. It is thown down as a pale pink powder practically insoluble in hot or cold water, and possessing in general the other properties of nickel tartrate. A sample of this dried at 120° gave 28.32 per cent. cobalt (theory, 28.49 per cent.).

When cobalt hydroxide is treated in the cold with tartaric acid it dissolves to a certain extent a pink solution resulting, which, on standing, deposits reddish pink crystalline scales of cobalt tartrate. This crystalline substance differs from the cobalt tartrate just described by being somewhat soluble in water. It is impossible to obtain as concentrated solutions of cobalt tartrate as of nickel tartrate, for the reason just mentioned, that some of the salt crystallizes out. With, however, as strong a solution as could be obtained the following determinations were made of the depression of the freezing-point.

TABLE 7.

Amount $CoC_4H_4O_6$ in 100 cc. solution. Gram.	Depression.	Apparent molecular weight.
0.6505	0.059°	207
0.3252	0.036	170
0.1626	0.021	146

Molecular weight of $CoC_4H_4O_6 = 207.1$.

These results run about the same as those obtained with solutions of nickel tartrate of similar concentration. The apparent molecular weight, 207, is very nearly equal to the molecular weight calculated from the formula; therefore, for the reasons already mentioned, the true molecular weight of cobalt tartrate is probably twice 207.1, which means its structure would be represented by twice the above formula or $(CoC_4H_4O_6)_2$. Table 8 gives the results of the determination of the electrical conductivity of solutions of this substance. The units are on the basis of equivalent ($\frac{1}{2}$ $CoC_4H_4O_6$) in a liter as before.

TABLE 8.

Temperature 18°.

m.	L.
0.0628	15.9
0.0314	22.1
0.0157	28.7
0.0079	37.6
0.0039	47.1
0.0020	58.4
0.0010	69.9
0.0005	82.1

These results are entirely analogous to the conductivity of nickel tartrate (Table 2). They are abnormally small and show that cobalt tartrate is only slightly dissociated, which affords additional evidence that the molecule is polymerized.

Cream tartar acts vigorously on cobalt carbonate in the presence of water, the resulting solution being colored a deep pink. When this solution is evaporated over sulphuric acid, reddish pink crystalline scales are deposited, very similar in appearance to the deposit from a solution of cobalt tartrate. When almost to dryness the solution assumes a pasty nature, and can be completely dried only with considerable difficulty. No salt of the formula, $K_2CoC_8H_8O_{12}$, could be isolated. The crystalline deposit just mentioned yielded on drying 24.53 per cent. cobalt,[1] and a small quantity of potassium was also found. The deposit, therefore, consists largely of cobalt tartrate, but a small amount of potassium tartrate is mixed with it. Watts' "Dictionary," and the others above cited, say that potassio-cobaltous tartrate forms large rhomboidal prisms. No such crystals could be obtained by any of the methods used here. Determinations of the freezing-point of solutions prepared from cream tartar and cobalt carbonate yielded essentially the same results as similar solutions prepared from nickel carbonate. Such results might well be in harmony with the separate existence in the solution of potassium tartrate and cobalt tartrate, so no definite knowledge of the nature of the molecules in solution could be obtained by this method. Heating this solution causes the precipitation of a light pink powder. After washing this and drying at 120°, 28.38 per cent. cobalt was found which showed it to be cobalt tartrate. This substance possesses all the properties and is apparently identical with the cobalt tartrate previously mentioned.[2] It is to be noted that the conduct of this solution on heating is somewhat different from that prepared from nickel carbonate and cream tartar, for a flocculent precipitate resulted on heating this latter to boiling.

When potassium hydroxide is added to a solution of cobalt tartrate the conduct is very similar to that when it is added to a solution of nickel tartrate. It differs, however, in this respect,

[1] The theoretical percentage of cobalt according to formula $K_2CoC_8H_8O_{12}$, is 13.61.

[2] That prepared by treating hot tartaric acid with cobalt hydroxide.

that when the quantities of potassium hydroxide and cobalt tartrate are in the proportion of one molecule of the former to one of the latter, instead of obtaining a gelatinous mass, a *flocculent precipitate* results, which readily dissolves on further addition of potassium hydroxide. The range of the existence of this precipitate is considerable; that is, it begins to form when the amounts of the two substances are in about the ratio of one-half molecule of potassium hydroxide to one of cobalt tartrate, and does not entirely disappear until the potassium hydroxide is present in about the ratio of $1\frac{1}{2}$ molecules to 1 of the cobalt tartrate. This seriously interfered with following the effect on the freezing-point of successive additions of potassium hydroxide to cobalt tartrate. There is no difficulty, however, in determining the freezing-point of the solution when the potassium hydroxide is present in the ratio of two molecules of it to one of the tartrate; the results thus obtained are given in Table 9.

TABLE 9.

Amount $CoC_4H_4O_6$ in 100 cc. solution. Gram.	Amount KOH added. Gram.	Depression.
0.6505	0.0000	0.061°
0.6505	0.4530	0.106

If the molecular weight is calculated from the depression 0.106°, it gives 159, while according to the formula, $K_2CoC_4H_2O_6$, the molecular weight is 283.3. Owing to the dissociation which such a salt would suffer in aqueous solution, it is very probable that it exists here in the solution, and that it is due to its formation that cobalt hydroxide cannot be precipitated by alkalies from a solution of a cobalt salt to which tartaric acid has been added. The precipitate above referred to, formed when the amount of potassium hydroxide added to the cobalt tartrate is in the ratio of one molecule of the former to one of the latter, was filtered off and washed until the wash-water was no longer alkaline. It was then dried and the cobalt in it determined. In one sample the percentage of cobalt was 42.78 and in another 38.04. The precipitate has, therefore, no definite composition, but undoubtedly contains some cobalt hydroxide, for no conceivable tartrate of cobalt has as great a percentage of cobalt as was found.

SOLUBLE NICKEL SULPHIDE.

It is evident that when investigating the effect of an alkaline tartrate solution in preventing the precipitation of nickel sulphide by hydrogen sulphide, it is desirable to exclude the presence of other chemical substances. Tartaric acid and sodium hydroxide were, consequently, not added to a solution of a nickel salt, as for instance the chloride, for this would produce some sodium chloride, whose influence on the precipitation with hydrogen sulphide would then be entirely unknown. Solutions of pure nickel tartrate were prepared as has already been indicated, and to this the alkali and hydrogen sulphide were then added. If it was desired to note the effect of any neutral salt, as sodium chloride, on the precipitation, such salt was added separately. All the nickel tartrate used was made from nickel nitrate, which was a preparation of Schuchardt's and was marked "*purissimum*." According to Villiers,[1] sodium hydroxide is more effective in holding nickel sulphide in solution than potassium hydroxide. Solutions of nickel tartrate were treated with one equivalent of sodium hydroxide,[2] with two equivalents of sodium hydroxide, with three equivalents, and so on. Hydrogen sulphide was run into these solutions to saturation and the solutions filtered. In the first solution nickel sulphide was precipitated and the filtrate was only slightly colored, in the second the filtrate was a decided brown, in the third it was black, but to be certain that no nickel sulphide is precipitated it is necessary to have at least five equivalents of sodium hydroxide to one of nickel tartrate. This black filtrate oxidizes with remarkable rapidity, which is shown by the continual separation of sulphur. It is apparently the sodium sulphide present, which thus suffers oxidation, but what is peculiar, is that the oxidation is more rapid than ever takes place in a solution of sodium sulphide alone. The more dilute the solution, the less marked is the oxidation. If this black alkaline solution of nickel sulphide is allowed to stand for an indefinite length of time, the nickel sulphide gradually precipitates, so that in from five to ten days the supernatant liquid has usually become clear.

[1] Compt. rend., 119, 1263 (1894).

[2] By an equivalent of sodium hydroxide is meant that quantity which bears a ratio to the nickel tartrate used of 2 molecules NaOH to 1 molecule $NiC_4H_4O_6$.

This settling can be greatly accelerated by the presence of a neutral salt, as sodium chloride or potassium sulphate, the time necessary for settling varying with the amount of such salt added. The presence of a large quantity of these salts before the introduction of hydrogen sulphide causes a large portion of the nickel sulphide to be precipitated.

The behavior of this black solution of nickel sulphide seemed to indicate that it is not a true solution, but colloidal in nature. To decide this several tests were applied. With a high-power microscope it was impossible to detect solid particles of any sort. The following test employed by Muthmann[1] was applied: It consists in treating the solution in question with a solution of gum-arabic, shaking well, and then adding alcohol to precipitate the gum. If the substance is a colloid, it is precipitated with the gum and colors it. Before applying this test it is necessary to assure one's self that alcohol will not produce a precipitate in the original solution. In this case if the alcohol did not exceed 50 per cent. of the total liquid, nothing was precipitated, so care was exercised not to add more than this amount. The gum when precipitated was colored black, and on standing a few hours the supernatant liquid became clear. The alcohol was then poured off, and the residue treated with water, which dissolved it up again, the solution being colored black as before. This is the typical behavior of a colloidal substance. Tyndall's experiment applied by Picton[2] to solutions of antimony and arsenic sulphides was tried with this solution. The method employed was essentially this: The liquid in question was placed in a small bottle and the bottle so supported that the rays from an arc light could be focused directly on its bottom. The light, which diffused from the side of the bottle, was examined through a nicol. A colloidal solution of arsenic sulphide was first examined to see that the apparatus gave proper results. The light was polarized, which is in harmony with the results of Picton and the later ones of Stoekl and Vanino.[3] The solution of nickel sulphide was then examined. On account of its dark color, it was necessary to use a very dilute solution so that the light would not be com-

[1] *Ber. d. chem. Ges.*, **20**, 983 (1887).
[2] *J. Chem. Soc.*, **61**, 143 (1892).
[3] *Ztschr. phys. Chem.*, **30**, 111 (1899).

pletely absorbed. With such a dilute solution no difficulty was experienced in getting it into the bottle, before the separation of any sulphur due to oxidation could take place. The light diffused from this solution was completely polarized. Some distilled water from which the solutions were made, was then placed in the bottle and examined in the same manner. No polarization could be detected. I am greatly indebted to Mr. H. W. Woodward of the physical department of this university for very efficient aid in these optical investigations. Independent observations by him in each one of the foregoing cases confirmed mine in every particular. All these tests, therefore, seem to show that nickel sulphide exists in an alkaline tartrate solution in the colloidal state; that is, as solid particles in an extremely finely divided condition, too small to be seen with any microscope but not so small but that they reflect light.

COBALT SULPHIDE.

Cobalt sulphide was produced in a manner exactly similar to that used in preparing soluble nickel sulphide. A solution of cobalt tartrate was made alkaline with a quantity of sodium hydroxide sufficient to hold nickel sulphide in solution, and then hydrogen sulphide run in to saturation. The cobalt tartrate was prepared from chemically pure cobalt chloride of Kahlbaum's, marked "*nickel frei.*" After the hydrogen sulphide had been run into the alkaline solution, it was filtered. According to Villiers, the cobalt sulphide is entirely precipitated, but in nearly every case the filtrate was colored brown. Villiers points out that by this method one can detect the presence of nickel in most preparations of cobalt supposedly free from nickel. It was, therefore, expected that the brown coloration just referred to was due to the presence of a trace of nickel. This brown filtrate was refiltered two or three times, then shaken with sodium chloride, and allowed to stand over night. In the morning a slight black sediment had deposited and the supernatant liquid was perfectly clear. The deposit was filtered off, washed and dissolved in aqua regia. After removing the excess of acid, acetic acid and potassium nitrite were added, and the mixture left twenty-four hours, at the end of which time a well-defined

yellow precipitate had appeared. This shows conclusively that the brown color of the alkaline solution was due to cobalt sulphide in solution and not nickel, for not a trace of nickel could be found in the filtrate from the nitrite precipitate. This experiment was repeated several times and nearly every time some cobalt sulphide went into solution. The presence of a moderate quantity of a neutral salt, will, however, insure complete precipitation of the cobalt sulphide.

CONCLUSION.

The difficulties attendant on the separation of nickel and cobalt by the method of Villiers are the following: The oxidation of the solution to which the hydrogen sulphide has been added results in the separation of so much sulphur, that if nickel is present and cobalt is not, the black solution will color the sulphur, making it very difficult to distinguish from precipitated cobalt sulphide. Furthermore, according to the process used in this separation, sodium chloride is present in the solution, and although this aids in the complete precipitation of cobalt sulphide, it may cause some nickel sulphide to be precipitated, which in the absence of cobalt sulphide might readily be mistaken for it.

The nickel sulphide in solution in an alkaline tartrate medium is in the colloidal state.

Of the different tartrates of nickel and cobalt investigated, the most interesting are the solutions of the tartrates of these metals prepared from their hydroxides and cold tartaric acid. The results of determinations of the lowering of the freezing-point and of the electrical conductivity are very exceptional for salts of this sort, and seem to point to the existence of a polymerized molecular structure.

The evidence seems to be pretty conclusive, that the cause of the non-precipitation of the hydroxides of nickel and cobalt from solutions of their tartrates, or at least that any precipitate that may form dissolves in excess of the reagent, is due to the formation of a compound in which these metals replace the hydrogen atoms of the alcoholic hydroxyl groups of tartaric acid.

WESTERN RESERVE UNIVERSITY,
CLEVELAND, OHIO, June, 1900.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 26.]

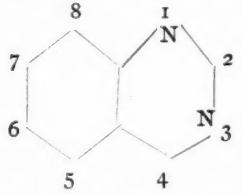
THE DIRECT SYNTHESIS OF KETODIHYDROQUINAZOLINS FROM ORTHOAMINO ACIDS.[1]

BY MARSTON TAYLOR BOGERT AND AUGUST HENRY GOTTHELF.

Received June 28, 1900.

AS announced in our preliminary paper on this subject,[2] ketodihydroquinazolins (or oxyquinazolins) can readily be obtained by the action of nitriles upon orthoamino acids under conditions of heat and pressure. The present paper is confined to a discussion of the 2-methyl-4-ketodihydroquinazolin. Many others have been prepared and studied, and will form the subjects of later communications.

For convenience, throughout this article we have called our compound a "quinazolon" although we do not intend thereby to indicate any preference for the keto form as compared with the tautomeric oxyquinazolin form. The numbering for the quinazolin nucleus is that first suggested by Paal and Busch.[3]



Weddige[4] the discoverer of this 2-methyl-4-ketodihydroquinazolin, obtained it from orthoacetaminobenzamide by fusion, by solution in alkalies with subsequent precipitation with acid, or by long boiling with water; also, by heating ethylorthoacetaminobenzoate to 160° C. with strong aqueous ammonia. Bischler and Burkart[5] accomplished the same result by fusing the ammonium salt of orthoacetaminobenzoic acid, while Niementowski[6] prepared it by heating together anthranilic acid and acetamide.

[1] Read before the joint meeting of the American Chemical Society and Section C of the American Association for the Advancement of Science, June 25, 1900.

[2] This Journal, **22**, 129.

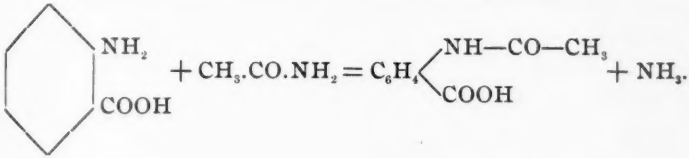
[3] *Ber. d. chem. Ges.*, **22**, 2684.

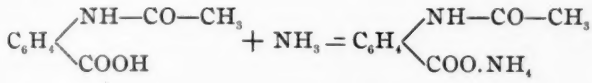
[4] *J. prakt. Chem.* [2], **31**, 124; **36**, 143.

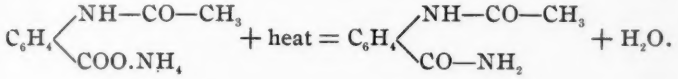
[5] *Ber. d. chem. Ges.*, **26**, 1350.

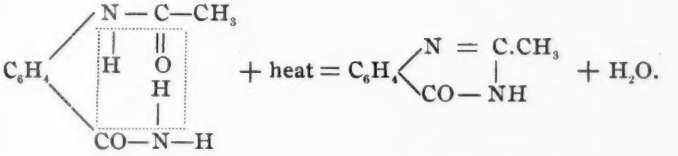
[6] *J. prakt. Chem.* [2], 51, 564.

The syntheses of Weddige and Bischler are practically identical, both depending upon the formation of orthoacetaminobenzamide, from which the quinazolon results by loss of water. The course of Niementowski's synthesis is probably similar in the main, the following reactions being suggested in explanation:



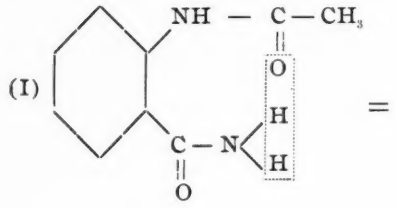


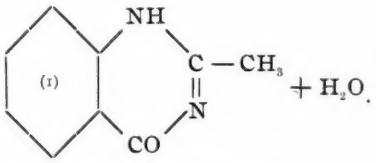




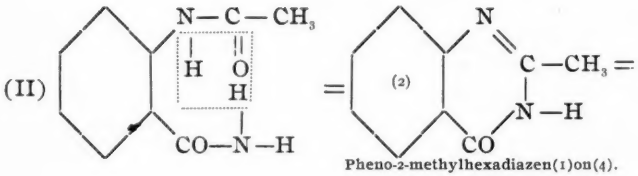
The first of these reactions seems probable when one remembers that acetanilide results from heating together aniline and acetamide, and that, with other amines, acetamide likewise yields the amide of the higher acid. The remaining reactions are then the same as in Bischler's synthesis.

In all these syntheses there is an interesting point which should not be overlooked, and that is the manner in which the water splits out in the production of the quinazolon. By an examination of the formulas, it will be seen that this may occur in two different ways, one being a lactam condensation, the other equivalent to a lactim condensation, resulting in the production of two separate and distinct isomers, as follows:

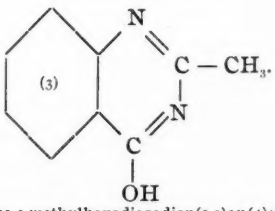




Pheno-2-methylhexadiazen(2)on(4).



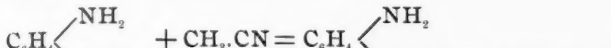
Pheno-2-methylhexadiazen(1)on(4).

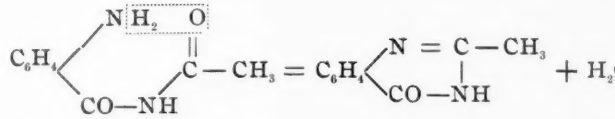


Pheno-2-methylhexadiazadien(1,3)on(4); or 2,methyl-4-oxyquinazolin.

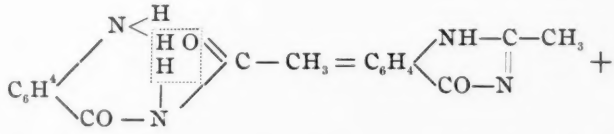
By a series of interesting reactions, Weddige proved his product to be (2) or (3), and the condensation, therefore, to have followed reaction (II). He did not, however, determine whether the compound appeared preferably in its keto or enol form, in his further studies of its properties. The products obtained by Bischler, by Niementowski, and by ourselves are identical in all respects with this compound of Weddige's, and the isomer represented by (1) is still unknown.

The conditions of our experiments resulting in the production of a quinazolon from anthranilic acid and nitriles were such that the first product of the reaction might be either a secondary amide, due to a condensation of the carboxyl and cyanogen groups or a transposition of groups might occur, giving anthranilic nitrile and acetic acid.[1] In the first case then, as our substance is identical with Weddige's, the reactions would be as follows:





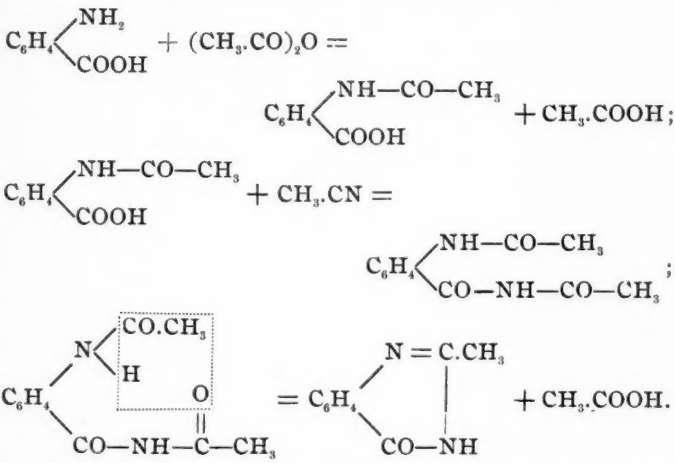
and not thus



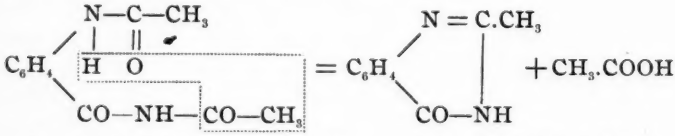
If this really represents the course of the reaction, it presents one or two interesting features. First, the elimination of water cannot here occur in the way described by Weddige, or an isomer would result with the double bond at (2) instead of at (1) as already mentioned. In regard to this point, however, it should be noted that this reaction is not exactly comparable with Weddige's, since in one case the condensation occurs with an aminic group, and in the other case with an amidic one. Another feature in which this synthesis differs from those already mentioned is in the position of the condensing acyl group, which here appears on the acid chain instead of in the amino group.

In later experiments, where acetic anhydride was present, the reactions would be similar:

[1] Compare Gautier: *Compt. rend.*, **67**, 1255; and Colby and Dodge: *Am. Chem. J.*, **13**, 1.

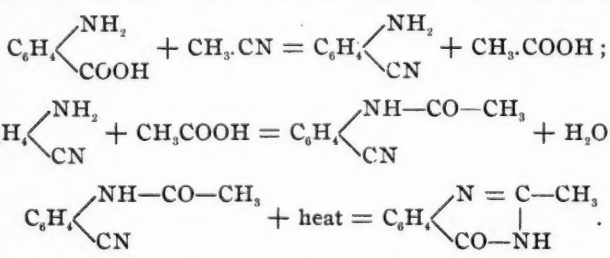


Although, in this case the possibility is not excluded of the reaction following the line indicated by Weddige:



In proof of the above reaction, acetylanthranilic acid was heated in a sealed tube with acetonitril, and the same quinazolon obtained.

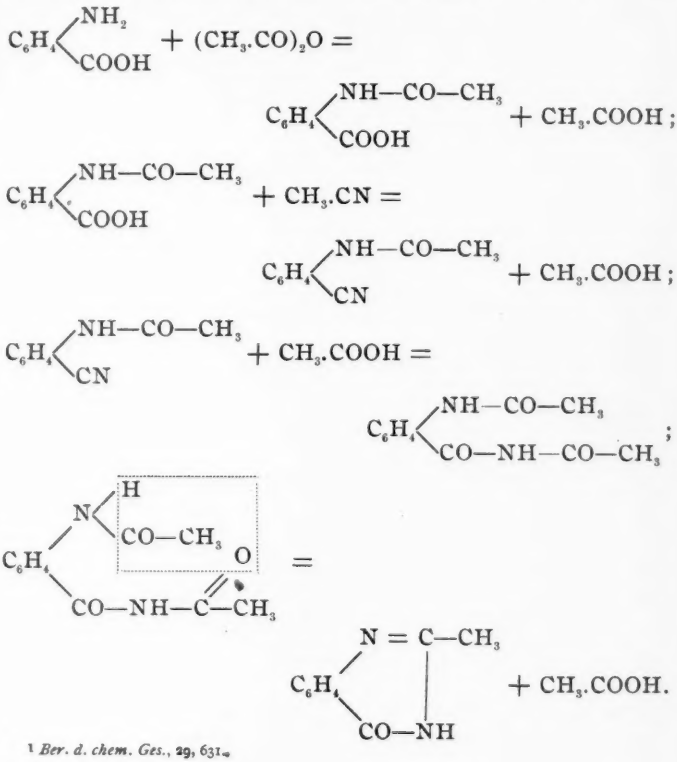
Another course which may be followed by the reaction is this:



The quinazolon being more stable at high temperatures than the anthranilic nitrile might cause such a rearrangement, but

Saemann,[1] who examined anthranilic nitrile, together with its acetyl and benzoyl derivatives, observed no such change. The production of anthranilic nitrile as the first phase of the reaction is more in accord with the results obtained by Colby and Dodge, but in some experiments carried out by us with the meta- and paraminobenzoic acids and acetonitrile we have been unable to isolate any aminobenzonitriles, although similar experiments with the three nitrobenzoic acids readily yielded the corresponding nitrobenzonitriles.

In our first experiments equal molecules of acid and nitrile were used, but in all of the later ones acetic anhydride was also added, and the reaction will then be slightly different:



[1] *Ber. d. chem. Ges.*, 29, 631.

We, therefore, prepared some acetylanthranilic nitrile and heated it with acetic anhydride in a sealed tube, the result being the same quinazolon as before. Such a reaction is not likely to have taken place in the tubes where no acetic anhydride was used, for there would have been no excess of acetic acid to combine with the nitrile for the production of the secondary amid, the acetic acid reacting first, of course, with the amino group.

To sum up then, it seems most probable to us that the course of the reactions is as follows:

1. *In Absence of Acetic Anhydride.*—Condensation of the carboxyl and cyanogen groups to a secondary amide, which passes into the quinazolon by loss of water.

2. *In Presence of Acetic Anhydride.*—Production of acetylanthranilic acid, with subsequent combination of carboxyl and cyanogen groups, the resulting secondary amide yielding the quinazolon by loss of acetic acid.

EXPERIMENTAL PART.

Synthesis of 2-methyl-4-ketodihydroquinazolin from anthranilic acid and acetonitrile.

Anthranilic Acid and Acetonitrile.—One molecule of anthranilic acid and 2 or 3 molecules of acetonitrile were heated together in a sealed tube for six hours at 200°–210° C. The tube then contained a crystalline mass wet with a dark liquid, and when opened evolved carbon dioxide with considerable force. The mass was extracted with ether, and the ether solution filtered. On driving off the ether from the filtrate a brown oil remained together with a small amount of a crystalline substance. This oil was driven over with steam and found to be aniline, while the crystalline substance was identified as acetanilide. The carbon dioxide and aniline were the usual decomposition products of the anthranilic acid, the acetanilide being formed by a secondary reaction between aniline and acetic acid or aniline and acetamide.

The residue insoluble in ether consisted of needles which, recrystallized from water and bone-blacked, melted at 232°–233° C. (238°–239° C. corr.). These crystals were insoluble in cold water, soluble in hot, and partly soluble in hot chloroform. The

aqueous solution was acid to litmus, but did not decompose sodium carbonate solution, or dissolve freshly precipitated silver oxide when boiled with it. They readily dissolved in concentrated potassium hydroxide solution, but underwent no decomposition when the solution was boiled; but when this same alkaline solution was boiled with excess of concentrated hydrochloric acid and then cooled, long transparent needles of a hydrochloric acid salt were obtained, which sublimed before melting and gave the free base again (m. p. 232° C.) when treated with sodium carbonate solution. An aqueous solution of the free base gave the following reactions: with copper sulphate solution, a light blue precipitate; with silver nitrate solution, a white precipitate; with stannous chloride solution, a gelatinous precipitate, dissolving on heating and separating out in needles on cooling; with cobalt nitrate solution, a voluminous curdy precipitate, blue in presence of any excess of alkali; with mercuric chloride solution, a curdy white precipitate; with lead acetate solution, a curdy white precipitate. An aqueous solution of the hydrochloric acid salt gave a dark yellow precipitate with neutral potassium chromate, and an orange-red one with platinum chloride.

The free base crystallizes from water in transparent prisms or needles, carrying 1 molecule of water of crystallization which they readily lose at 100° C. An analysis of the crystals, dried at 100° C. gave the following results:

I. 0.1582 gram substance gave 0.3904 gram carbon dioxide, and 0.0711 gram water.

II. 0.1584 gram substance gave 0.3898 gram carbon dioxide, and 0.0722 gram water.

III. 0.1466 gram substance gave 0.3628 gram carbon dioxide, and 0.0666 gram water.

IV. 0.1613 gram substance gave 26 cc. nitrogen at 24° C. and 756 mm.

V. 0.1468 gram substance gave 23.8 cc. nitrogen at 22.5° C. and 750 mm.

	Calculated for $C_9H_8N_2O$.	Found. I.	II.	III.	IV.	V.
Carbon	67.50	67.30	67.11	67.49	....	....
Hydrogen	5.00	4.99	5.06	5.04	....	....
Nitrogen	17.50	....	....	....	17.97	18.07
Oxygen	10.00	....	....	....	....	....
	100.00					

The molecular weight was also determined by the freezing-point method, using glacial acetic acid as the solvent:

Weight of substance taken	0.3184 gram.
" " glacial acetic acid	23.7600 grams.
Freezing-point of acetic acid	4.05°
" " " mixture	3.71°
Lowering of freezing-point	0.34°
K	3880.0
Molecular weight	153.0
" " of $C_9H_8N_2O$	160.0

The substance is hence identical with the 2-methyl-4-ketodihydroquinazolin of Weddige, Bischler, and Niementowski.

One of the first difficulties encountered in this synthesis is the tendency of the anthranilic acid to break up into carbon dioxide and aniline, and we have not been able as yet to overcome this entirely. Very gradual heating of the tube contents, even when long continued, did not appear to give any better yield than direct heating at 200°–210° C. for six or eight hours. The water split off in the reaction was also found to exert a most harmful influence upon the products, causing decomposition and the formation of much tar. The use of an excess of acetonitrile improved the yield somewhat, and the addition of acetic anhydride was found particularly beneficial in this respect. By using nearly enough anhydride to take up all the water split off, the yield was nearly doubled, being brought up to 45 per cent. of the theory, while the tube contents were invariably light colored and free from tar.

Syntheses of Bischler and Burkart, and of Niementowski.—For purposes of comparison some 2-methyl-4-ketodihydroquinazolin was prepared by the method of Bischler and Burkart, and of Niementowski.

Bischler and Burkart's Synthesis.—Acetylanthranilic acid was neutralized with ammonia, the solution evaporated to crystals, and the product recrystallized. Fusion of these crystals for twenty minutes gave a yield of the quinazolon amounting to about 25 per cent. of the weight of the acetylanthranilic acid used. Dehoff,[1] who was the first to suggest this method, abandoned it as unsatisfactory, but his difficulty seems to have been in getting a pure anthranilic acid to start with.

[1] *J. prakt. Chem.* [2], 42, 347.

Niementowski's Synthesis.—This investigator states that by fusing together acetamide and anthranilic acid for six to eight hours at 135°–155° C. a yield of quinazolon may be obtained equal to half the weight of the anthranilic acid used. Our experience indicated that twenty-four hours' heating at this temperature was necessary to remove all ammonia, and the yield of quinazolon was only about half that given by Niementowski. By treating the melt with ether the quinazolon remains insoluble and can thus be separated and recrystallized. In the ethereal washings we have isolated, in addition to acetanilide, a substance crystallizing from water in flat needles with jagged edges, and melting at 190°–191° C. (194°–195° C. corr.). This melting-point could not be altered by repeated crystallizations, from water, and the substance cannot therefore be impure quinazolon. With metallic potassium or sodium the presence of nitrogen in this substance is easily demonstrated, but boiling with concentrated potassium hydroxide solution produces no ammonia, aniline, or other primary amine, for no isonitrile odor could be detected after the addition of chloroform, and it does not seem possible, therefore, that the compound can be amidic in character. That it probably represents an intermediate step in the reaction, however, is clearly shown by the fact that it can be converted to the quinazolon by boiling with concentrated hydrochloric acid or by sublimation. We are now endeavoring to prepare sufficient of this material to determine its structure, in the hope that it may throw considerable light upon the course of this interesting synthesis.

PREPARATION OF DERIVATIVES OF 2-METHYL-4-KETODIHYDROQUINAZOLIN.

Three sets of derivatives were prepared for purposes of comparison, one from quinazolon obtained by Bischler's synthesis, another from quinazolon obtained by Niementowski's synthesis, and a third set from our own product. An examination of similar derivatives in the three sets showed them in every case to be identical in all points irrespective of the source of the quinazolon.

Hydrochloride.—Prepared by boiling the free base, or its alkaline salts, with excess of concentrated hydrochloric acid. As the solution cools the hydrochloride crystallizes out in long trans-

parent needles, often of a decided yellowish cast and with a strong greenish fluorescence. These needles sublime without decomposition or dissociation, and do not break up at 336° C. as reported by Niementowski.[1]

Chlorplatinate.—By the addition of platinic chloride to a hot solution of the hydrochloride the chlorplatinate gradually separates on cooling in coarse red crystals, which can be recrystallized from water. Frequently unchanged hydrochloride will persistently separate with the chlorplatinate even after prolonged boiling with excess of platinum chloride.

	Calculated for $(C_9H_8N_2O.HCl)_2PtCl_4$.	Found. I.	II.
Pt	26.61	26.62	26.78

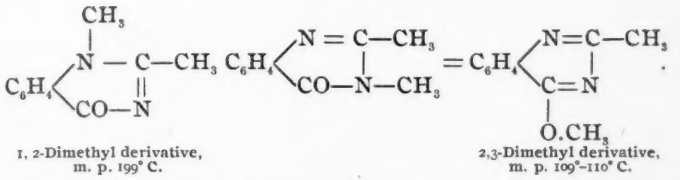
Nitrate.—When the free base is boiled with an excess of nitric acid (1 : 4), and the solution allowed to cool, the nitrate separates in white needles, which decompose at about 185° C. Niementowski found his product to decompose at 195° C.

Chromate.—This salt was prepared both by the addition of potassium chromate to a solution of the hydrochloride, and also by heating the free base with chromic anhydride. It forms yellow crystals, beginning to blacken at 176° C. rather than at 182° C. as reported by Niementowski.

	Calculated for $C_9H_8N_2O.CrO_3$.	Found.
Cr	20.00	19.41

Methyl Ether.—Equal molecules of 2-methyl-4-ketodihydroquinazolin, potassium hydroxide, and methyl iodide are dissolved in alcohol, and the mixture heated several hours on the water-bath with a return condenser. The alcohol is driven off, and the residue crystallized from water. It then forms white needles, melting at 71° C. (72° C. corr.) in the hydrated condition, and at 109°–110° C. (110°–111° C. corr.) when anhydrous, thus identifying it with the β,γ-dimethyl-Δ-pseudoxyquinazoline of Weddige,[2] and proving conclusively the structure of the original 2-methyl-4-ketodihydroquinazolin, for the isomeric pheno-2-methylhexadiazen(2)on(4) yields a dimethyl derivative melting at 199° C. The structure of these isomeric dimethyl derivatives is as follows:

[1] *Ber. d. chem. Ges.*, **29**, 1360.
[2] *J. prakt. Chem.* [2], **36**, 151.



1, 2-Dimethyl derivative, m. p. 199° C.

2,3-Dimethyl derivative, m. p. 109°–110° C.

It seems most likely, in view of recent work upon similar compounds, that the 2-methyl-4-ketodihydroquinazolin reacts with alkalies in its pseudo or enolic form, and that the dimethyl derivative mentioned above contains the second methyl group attached to oxygen and not to nitrogen, thus giving an ether of a true methyl quinazolin. This would also explain why the 2,3-dimethyl derivative has a melting-point so much lower than its isomer, for in the 2-methyl-4-ketodihydroquinazolin compound with the double bond at (2) the carbonyl is para to the imido group, and it could not therefore so easily pass into a pseudo-enolic form.

SYNTHESIS OF 2-METHYL-4-KETODIHYDROQUINAZOLIN FROM ACETYLANTHRANILIC ACID.

Acetylanthranilic Acid.—This was prepared by the method of Jackson,[1] from anthranilic acid and acetic anhydride. Anthranilic acid was boiled for three hours with twice the theoretical amount of acetic anhydride. On cooling nothing separated, so the mixture was precipitated by pouring into water, the mass then warmed slightly to decompose any excess of anhydride, and the precipitate filtered out and washed. This precipitate was next dissolved in ammonia water, reprecipitated by hydrochloric acid, the precipitate filtered out and crystallized from water, when it formed plates melting at 182°–184° C. Occasionally it separated in a gelatinous mass on crystallization, showing a slightly lower melting-point (181°–183° C.), due possibly to difficulty in getting it perfectly dry.

In all cases, a small amount of the precipitate obtained by the addition of hydrochloric acid to the ammoniacal solution refused to dissolve in boiling water. This insoluble portion was separated and crystallized from glacial acetic acid, yielding fine white needles, melting at 221°–223° C. This is probably the diacetyl

[1] *Ber. d. chem. Ges.*, **14**, 886.

derivative, but not enough was obtained for further investigation. Jackson,[1] reports similar results in his preparation of the acetylanthranilic acid.

Diacetylanthranilic Acid.—Bedson[2] states that when acetic anhydride and anthranilic acid are boiled together for some time under a return condenser the mixture solidifies on cooling to a crystalline mass of diacetylanthranilic acid. We have been unable to confirm this, as was the case apparently with Jackson also.

Anthranilic acid was boiled for several hours with acetic anhydride under a return condenser, but nothing separated on cooling. On addition of water a precipitate was obtained which, on recrystallization, proved to be impure monacetylanthranilic acid, melting at 175°–185° C. Another portion of anthranilic acid was heated with acetic anhydride until all excess of anhydride had been driven off. The residue was then dissolved in alcohol, the solution bone-blacked and evaporated, leaving a tarry mass from which hot benzene extracted a substance melting at 178°–182° C. on recrystallization, and which was evidently only impure monacetylanthranilic acid. Monacetylanthranilic acid was then boiled for ten hours with acetic anhydride, decomposition apparently setting in at this point, for when the mass was poured into water it produced a yellow milky solution with much tar.

The effect of pressure was next tried. Five grams of anthranilic acid, 9 cc. of acetic anhydride, and 10 cc. glacial acetic acid, were heated together in a sealed tube for five hours at 160°–170° C. The contents of the tube then appeared liquid, and no pressure was detected on opening the tube. The excess of acetic acid and anhydride was removed by distillation, and the residue left in a desiccator over potassium hydroxide, where it gradually solidified to a crystalline mass, some of which recrystallized from benzene melted at 180°–182° C. and proved to be the monacetyl derivative again. We have, therefore, failed to get any appreciable amount of diacetylanthranilic acid by the methods employed.

Acetylanthranilic Acid and Acetonitrile.—Five grams of acetylanthranilic acid and 7 cc. acetonitrile were heated together in a sealed tube for four and a half hours at 220°–210° C. The tube

[1] *Loc. cit.*

[2] *J. Chem. Soc.*, 37, 756.

was then filled with needle crystals and a dark brown liquid. No pressure was evident upon opening the tube. The liquid was decanted carefully from the crystals and the latter washed with dilute sodium carbonate solution, to remove unchanged acid, etc. The residual crystals dissolved in alcohol, bone-blacked, and the solution evaporated, yielded coarse needles melting at 232°–236° C. and readily identified with the 2-methyl-4-ketodihydroquinazolin prepared by the methods already mentioned.

To prove that no acetyl derivative of the quinazolon was produced in this reaction, 0.5 gram of the quinazolon was boiled for one hour with 5 cc. acetic anhydride, and on cooling long needles separated exactly similar to those obtained from the above reaction. That these were really only the original quinazolon was shown by the molecular weight determination, by the freezing-point method, with glacial acid as the solvent:

Weight of substance	0.4637 gram.
" " acetic acid	23.3805 grams.
Freezing-point of acetic acid	4.04°
" " " mixture	3.57°
Lowering of freezing-point	0.47°
K	3880.0
Molecular weight	163.7
" " of $C_9H_8N_2O$	160.0
" " " $C_9H_7N_2O(CO.CH_3)$	202.0

Acetyl chloride was found to have no action upon the quinazolon under ordinary conditions.

The experiments with anthranilic nitrile, acetylanthranilic nitrile, and similar orthoaminonitriles, form the subject of another paper.

In conclusion, then, the following new syntheses of 2-methyl-4-ketodihydroquinazolin have been discovered:

1. By heating orthoamino acids, or their acyl derivatives, with nitriles.

2. By heating orthoaminonitriles, or their acyl derivatives, with acids.

The extension of these syntheses to other acids and nitriles is now under way. We are also studying the action of nitriles upon α- and β-amino acids and their nitriles both aliphatic and aromatic, as well as the action of nitriles upon other classes of orthosubstituted acids.

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COLUMBIA UNIVERSITY, June 15, 1900.

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